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David W. Lipp

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SYNTHESIS AND CHARACTERIZATION OF  
PERHALOGENATED BROMOACETALDEHYDE POLYMERS

A Dissertation Presented

by

David W. Lipp

Submitted to the Graduate School of the  
University of Massachusetts in Partial  
Fulfillment of the Requirements for the

Degree of

Doctor of Philosophy

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Major Subject: Polymer Science and Engineering



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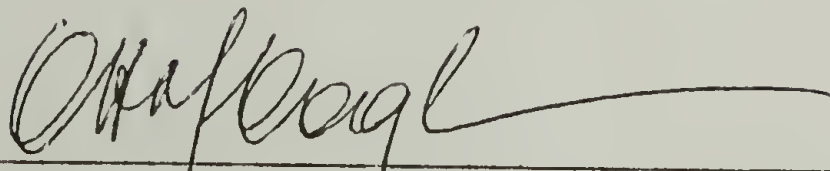
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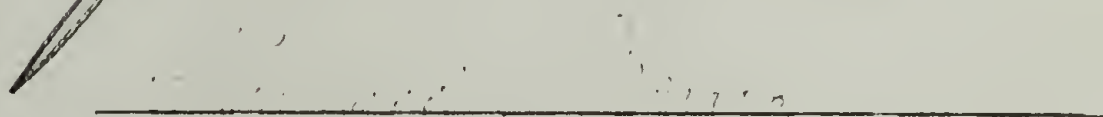
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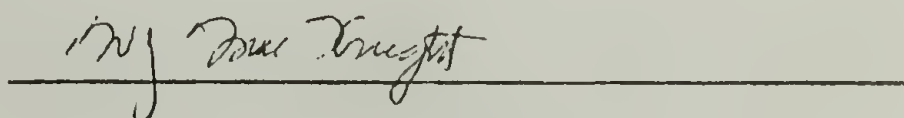
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## ABSTRACT

### Synthesis and Characterization of Perhalogenated Bromoacetaldehyde Polymers

(May, 1977)

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Directed by: Professor Otto Vogl

Bromodichloroacetaldehyde and Chlorodibromoacetaldehyde were synthesized and characterized by elemental analysis, I.R. spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. These two aldehydes and tribromoacetaldehyde were homopolymerized in the presence of nucleophiles and certain acids, to give high molecular weight polymers which were insoluble in all solvents tested. Characterization of these homopolymers by elemental analysis, I.R. spectroscopy, and thermal degradations indicated that they were linear substituted polyoxymethylenes with structures closely resembling isotactic polychloral. The threshold polymerization temperatures (1 molar solution of monomer in toluene) were determined by an instrumental technique to be: chloral +  $18^\circ\text{C}$  bromodichloroacetaldehyde -  $11^\circ\text{C}$  chlorodibromoacetaldehyde -  $43^\circ\text{C}$ , and tribromoacetaldehyde -  $75^\circ\text{C} \pm 2^\circ\text{C}$ . The thermal stabilities were determined by DTG analysis and all homopolymers prepared with nucleophilic initiation degraded to monomer quantitatively around  $150^\circ\text{C}$  while the homopolymers prepared

with acidic initiators were stable up to 200°C. The homopolymers could be stabilized by treatment with  $\text{PCl}_5$  and the degradation temperatures for stabilized samples were above 250°C. Stabilized homopolymers, by DSC, showed no significant transitions below the degradation temperatures. All of the homopolymers were semi-crystalline and showed X-ray scattering patterns which closely resembled X-ray patterns for polychloral. Low angle polarized light scattering patterns from films of polychloral and polybromodichloroacetaldehyde indicated a rod-like morphology and superstructure.

Bromodichloroacetaldehyde, chlorodibromoacetaldehyde and bromal were copolymerized with aryl and alkyl isocyanates. The comonomer content was characterized by I.R spectroscopy and elemental analysis and it was found that bromal was more reactive than chlorodibromoacetaldehyde which was more reactive than bromodichloroacetaldehyde in copolymerizations with isocyanates. A 1:1 copolymer of bromal and phenylisocyanate was prepared. These isocyanate copolymers degraded at temperatures between 200°C and 280°C by DTG analysis and they showed no transitions below these temperatures by DSC analysis. Bromal, bromodichloroacetaldehyde, and chlorodibromoacetaldehyde copolymerized with chloral and the copolymers were insoluble semi-crystalline and resembled isotactic polychloral. It was concluded that the 3 brominated aldehydes formed polymers which were very similar to isotactic polychloral. Stereoregular polymers were obtained in the presence of non-stereoregulating initiators; the bulky side groups allowed only successive meso additions to the growing polyaldehyde chains to form isotactic helical molecules under all reaction conditions.

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## INTRODUCTION

### A. Background

The polymerization of  $\alpha$ -olefins and vinyl ethers can be carried out under certain conditions to give polymers with well defined and uniform stereochemistry along the polymer chains. In principle, a new chiral center is formed upon each addition of a new monomer unit during the formation of the polymer chain. Most stereoregular polymers have their side groups arranged in a meso configuration along the polymer chain and these polymers are called isotactic polymers. Syndiotactic polymers are less common and have been only described for polypropylene, poly- $\alpha$ -methylstyrenes, poly  $\alpha$ -chloroacrylates, poly(vinyl-chloride), a few propenyl ethers, and poly (methylmethacrylate).

Stereospecific polymerization of  $\alpha$ -olefins and vinyl ethers require the use of transition metal initiators of complex structure with or without additional promoters or co-initiators. Sometimes bimetallic complexes have been described as the most effective initiators. The effectiveness of complicated transition metal initiators depends on



the capability of the transition metal to expand its orbitals and form unstable coordination complexes with olefins in which the olefin is brought to the reaction site in a stereoregular configuration. To some extent the electron density and size of the side group and polarization of the olefinic double bond play a role in the determination of the ultimate stereoregularity of the polymer chain. It is however, believed that the primary responsibility for most stereoregular polymerization of olefins and vinyl ethers rests on the stereoregulating capability of the transition metal complexes and the stereospecificity of this complex in the transition state of the growing chain.

Stereoregulation may also occur in ring opening polymerization of substituted cyclic ethers, particularly the polymerization of epoxides. The examples here are the polymerization of propylene oxide, and to some extent of phenyl glycidyl ethers. The stereoelecticity in cyclic ether polymerization is somewhat different than that of the carbon-carbon bond opening polymerization of  $\alpha$ -olefins. In the case of propylene oxide the polymerization consists of a stereoelection of one enantiomer over the other. The final result however is the same as in other stereospecific

polymerizations: the formation of stereoregular usually isotactic polymers. The most effective initiators for the stereoelective polymerization of propylene oxide were modified aluminum alkyl/water or alcohol systems or zinc alkyl/water or alcohol systems sometimes modified with aromatic amines or carbonyl compounds. These initiator systems were used with or without the use of epichlorohydrin as promoter.

Shortly after the discovery of stereoregular polymers of olefins, vinyl ethers, and propylene oxide it was discovered that acetaldehyde and other aliphatic aldehydes were capable of undergoing stereospecific polymerization to yield what was later found to be isotactic polymers. Isotactic polyacetaldehyde was obtained with alkali metal oxides, in an anionic polymerization, and with  $\text{BF}_3$ -etherate in a cationic polymerization. Very effective initiation was obtained with alkali metal oxides, in an anionic polymerization, and with  $\text{BF}_3$ etherate in a cationic polymerization. Very effective initiators for the polymerization of acetaldehyde and other higher aliphatic aldehydes were aluminum alkyl based initiators which were modified with a variety of alcohols and amines. Alcohols and amines with

responsible for the polymerization to isotactic polymers in cases where coordination of the monomer is not an essential part of the propagation step. Halogenated acetaldehydes containing side groups of various sizes were expected to polymerize under essentially the same conditions in all cases. Fluorine, chlorine, and bromine substituents would give side groups of increasing size and these side groups could affect the polymerizability of these compounds. It was recognized however that the inductive effects of the individual halogens and their polarizabilities could affect the electron density and charge distribution in the carbonyl group which might influence the polymerizability of these compounds.

Aldehydes with side groups larger than trichloromethyl have not been polymerized. Although efforts have been made in the past to polymerize bromal, all efforts have failed. It was believed that either the side group of bromal was too large to be accommodated in a polymer chain or that an impurity still remained in bromal even after careful purification which prevented its polymerization.

This work was consequently undertaken to prepare

polymer grade dichlorobromoacetaldehyde and dibromochloroacetaldehyde, to develop techniques for the polymerization of these two aldehydes, to find new techniques for the purification and possible polymerization of bromal itself, and to study the influence of the side group size on the stereoregularity of the polymers obtained.



## B. Preparation and Properties of Haloacetaldehydes

### 1. Chloroacetaldehydes

Chloral was first prepared by Liebig in 1832.<sup>(1)</sup>

Dichloroacetaldehyde and monochloroacetaldehyde have also been reported in the literature.<sup>(2-3)</sup> The chlorinated acetaldehydes have been important chemical intermediates for many years and several processes have been developed for the synthesis of these compounds.

## A. Preparation of Chloral

The most important syntheses of chloral involve the chlorination of ethanol,<sup>(4-20)</sup> or the chlorination of acetaldehyde.<sup>(20-36)</sup>

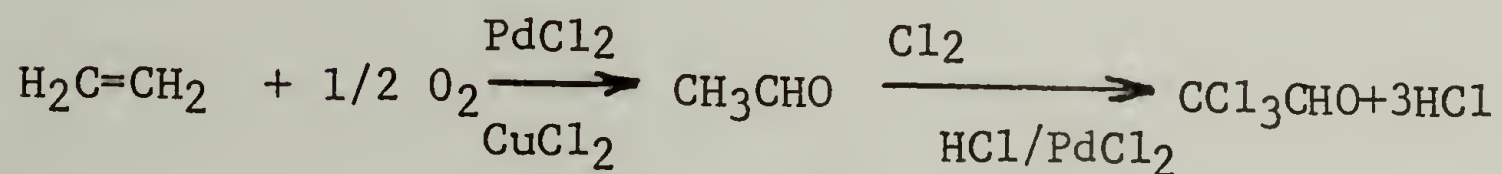
### 1. From Ethanol

Ethanol is chlorinated with elemental chlorine at 200°C in an inert solvent. Actually the alcohol function is oxidized to the aldehyde and the chlorination proceeds via acetals of acetaldehyde chloroacetaldehyde and chloroethers, chlorination giving chloral. Chloral has been purified by treatment with concentrated H<sub>2</sub>SO<sub>4</sub>, and distillation from H<sub>2</sub>SO<sub>4</sub> at 25°C and 50 mm pressure.<sup>(17-20)</sup> In one large scale process the chlorination was carried

out under irradiation in two stages. ( 15 )

## 2. From Acetaldehyde

Chloral has been synthesized in a two step process from ethylene where acetaldehyde is produced in the first step or in a one step process from acetaldehyde itself. In the two step process (35, 39, 41) HCl was oxidized to chlorine and the ethylene was converted to acetaldehyde which was then chlorinated.



The last step is not simple because HCl is a catalyst for the condensation reactions of acetaldehyde and it is easy to obtain chlorination products of crotonaldehyde.

(27, 28) There are several patents on the synthesis of chloral from acetaldehyde in a one step process. (21-32)

Paraldehyde, the trimer of acetaldehyde has also been chlorinated to chloral; in one process (30-32) the chlorination was carried out in the presence of  $\text{SbCl}_3$  and a second process (35) uses  $\text{CuCl}_2$ ,  $\text{LiCl}$  and  $\text{Cu}(\text{OAc})_2$  as catalysts for the chlorination.

## B. Preparation of Dichloroacetaldehyde

Dichloroacetaldehyde was obtained by chlorination of acetaldehyde or chlorination of ethanol.

### 1. From Acetaldehyde

Acetaldehyde was chlorinated under ultra-violet irradiation at 20-30°C until the density was 1.489. The reaction mixture contained mainly dichloroacetaldehyde in polymeric form which was thermally degraded.<sup>(21)</sup> Mon-chloroacetaldehyde was a by-product of this chlorination; its formation could be suppressed by adding organic sulfonic acids. Trichloroacetic acid was found to be a good solvent for the chlorination of acetaldehyde to dichloroacetaldehyde.<sup>(24, 25)</sup>

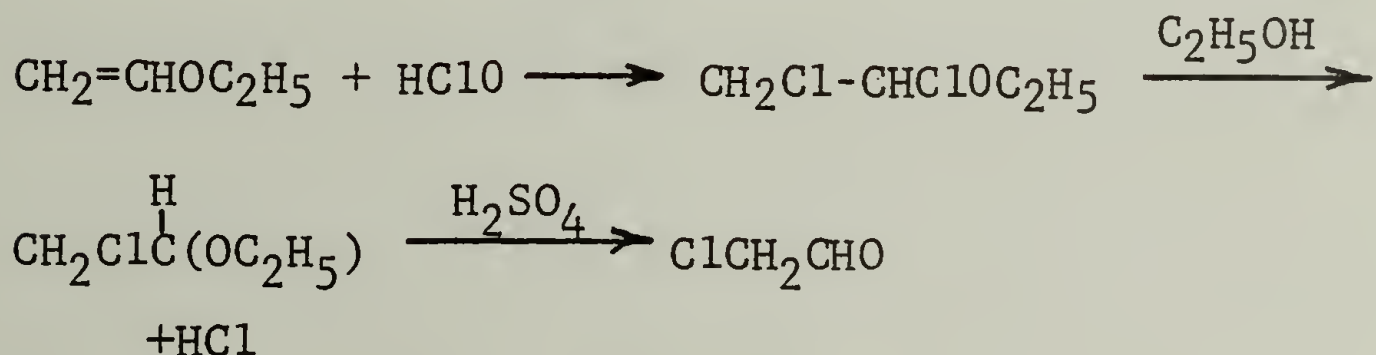
### 2. From Ethanol

Dichloroacetaldehyde has been obtained by the chlorination of ethanol in the form of the acetal<sup>(4)</sup> when ethanol was saturated with chlorine at 10-35°.<sup>(4)</sup> Ethanol could also be chlorinated in the vapor phase in the presence of an electric discharge.<sup>(7, 8)</sup> Almost all preparations of dichloroacetaldehyde which were obtained by chlorination of ethanol or acetaldehyde contained chloral.

A synthesis of pure dichloroacetaldehyde has been recently achieved by hypochlorination of trans-1,2-dichloroethane in dioxane (which was free of chloral).

### C. Preparation of Chloroacetaldehyde

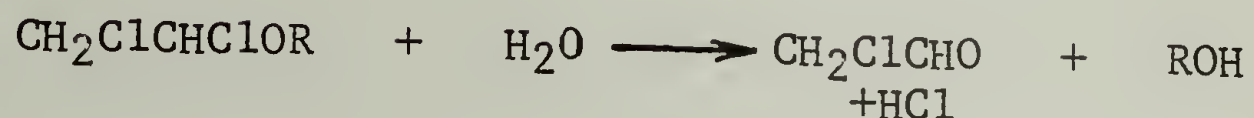
Appreciable amounts of monochloroacetaldehyde could be isolated from technical acetaldehyde when it was prepared by oxidation of ethylene with  $\text{PdCl}_2\text{-CuCl}_2$  catalysts. (39-41) Direct chlorination, under anhydrous conditions of paraldehyde has been reported. (42-46) Monochloroacetaldehyde was also prepared as the diethylacetal by the addition of chlorine or hypochlorous acid to vinyl ethers or vinyl esters at low temperatures in the presence of ethanol. (47-54) The free aldehyde may be obtained by treatment of the diethyl acetal from  $\text{H}_2\text{SO}_4$ . (52-60) ✓



Also chlorination of mixtures of acetaldehyde and alcohols gave readily 1,2-dichloroethylalkyl ethers which on



treatment with water gave monochloroacetaldehyde. (45)



Other processes involved the addition of water during chlorination. (9-14) Ethanol has also been chlorinated in the vapor phase with an electric discharge. (7, 8)

## 2. Bromoacetaldehydes

Brominated acetaldehydes have been known for a long time ever since Lowig reported a synthesis of bromal in 1832. (57) Most of the syntheses reported for bromoacetaldehydes involve the bromination of ethanol or acetaldehyde. (58)

### A. Preparation of Bromal

Organic Synthesis (59) contains a standard procedure for the preparation of bromal from paraldehyde. The paraldehyde is added to a mixture of bromine and a small quantity of sulfur to give bromal a 55% yield. Lowig synthesized bromal by brominating ethanol or by brominating diethyl ether in the presence of HBr. (57) Bromal has been prepared industrially by treating chloral with  $\text{AlBr}_3$  in hexane at  $60^\circ\text{C}$ . (60)

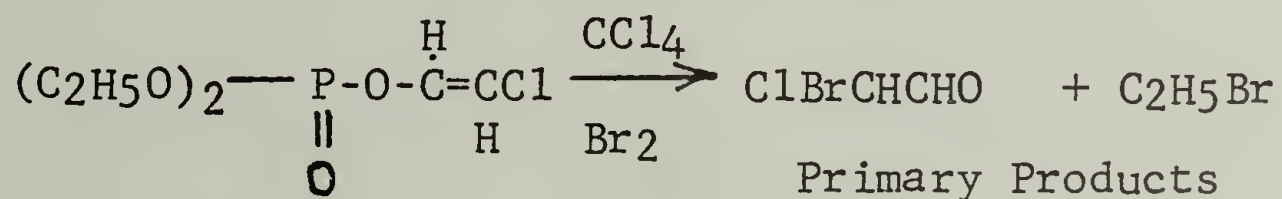
B. Preparation of Dibromoacetaldehyde and Monobromoacetaldehyde

Dibromoacetaldehyde has been prepared by treating acetaldehyde with bromine at 25-40 C° in chloroform, (61) and by treating paraldehyde with bromine in chloroform. (62) Bromoacetaldehyde has been prepared by brominating acetaldehyde with bromine in chloroform at low temperatures below 5°C, (63) and by reacting acetaldehyde with bromine in the presence of mercury. (64)

3. Preparation of Bromoacetaldehydes Containing a Second Halogen

a. Bromochloroacetaldehyde

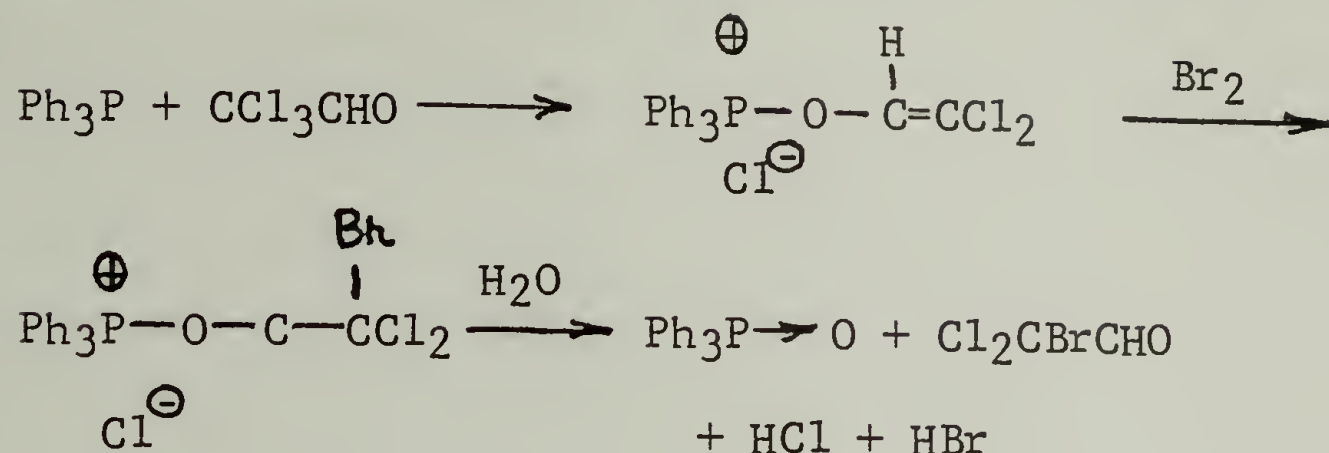
Addition of bromine to an equimolar quantity of diethyl 2-chlorovinyl phosphate in CCl<sub>4</sub> yielded 5% of diethyl 1,2 dibromo-2-chloro-ethyl phosphate and considerable quantities of unexpected products. Ethyl bromide and bromochloroacetaldehyde were produced. (65)



b. Other Aldehydes

Bromodichloroacetaldehyde was synthesized in a three

step sequence recently but no details were given. (66)



A 1954 patent claims the synthesis of  $\text{F}_2\text{CBrCHO}$  (67) but  $\text{Br}_2\text{CClCHO}$ ,  $\text{FBr}_2\text{CCHO}$  and  $\text{BrClFCHO}$  have not been reported.

### C. Haloacetaldehyde Polymers

Homopolymers of fluoral, chloral, dichloroacetaldehyde, chloroacetaldehyde, dibromoacetaldehyde and difluorochloroacetaldehyde have been described. Polychloral was discovered first, in 1832, and is one of the oldest known polymers. The synthesis of these polymers and their physical properties are described below.

#### 1. Chloroacetaldehyde Polymers.

##### A. Polychloral

Chloral will polymerize when initiated with anions, with certain acids, and with certain organometallic compounds. The polymerization initiated with anions have

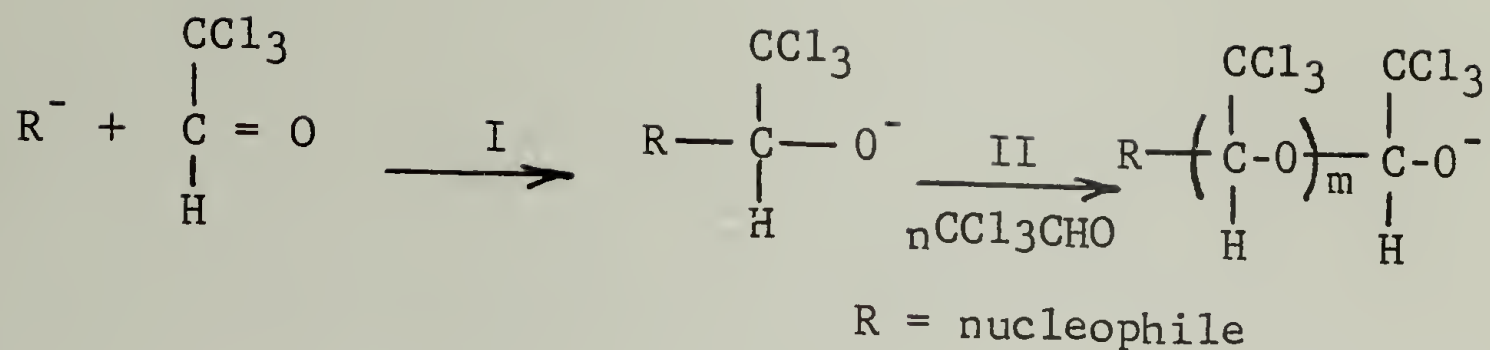
been studied the most extensively and will therefore be reviewed first.

(1) Polymerization of Chloral in the Presence of Anionic Initiators

Chloral polymerized rapidly to high conversion with a wide range of nucleophiles.<sup>(69, 73, 73, 75)</sup> These initiators included ammonium, phosphonium and sulfonium halides or carboxylates, tertiary amines and tertiary phosphines. Alkali metal and alkaline earth methyl alkyls, alkoxides, carboxylates, and halides were good initiators.<sup>(69)</sup> They must either be soluble in chloral or be solubilized in chloral with a complexing agent or diluent.

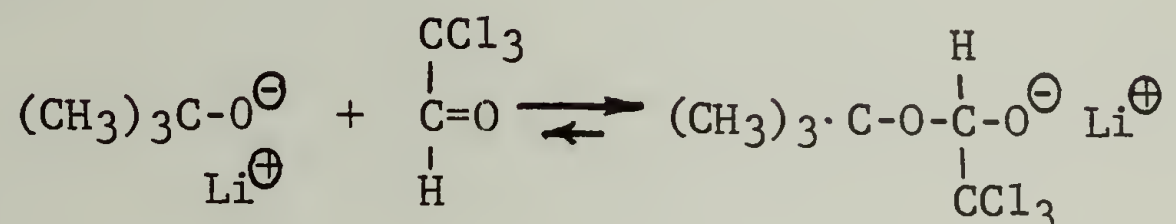
Coherent objects of polychloral of predetermined shape have been made if initiation occurred above the polymerization threshold temperature. A monomer casting process was developed called cryotachensic polymerization which consists of two separate and distinct steps.<sup>(68)</sup> In the first step the anionic initiator is added to monomer that has been heated above the polymerization threshold temperature. This temperature is 18°C for a 1 M solution of chloral in methyl cyclohexane and is 58°C for pure chloral.



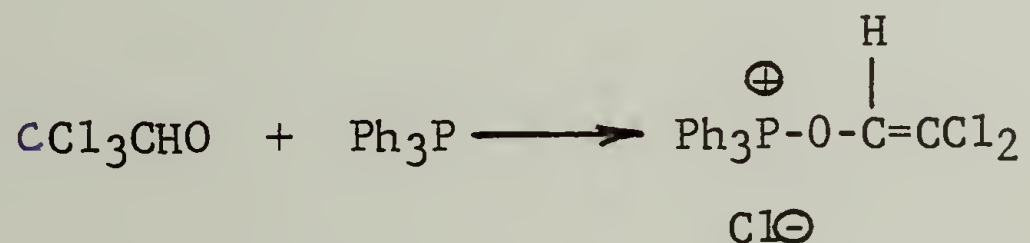


All of the anionic initiators were satisfactory for this process of initiation. The initiator may add one monomer unit but no propagation will occur. When the mixture is cooled below the threshold temperature the heat is removed, propagation occurs immediately. The polymerization proceeds as fast as the heat is removed. The polymerization is self controlling: if the internal temperature of the reacting mixture approaches the threshold temperature the polymerization slows down. If the initiated monomer is cooled under quiescent conditions, a self supporting gel is formed which hardens as the polymerization proceeds. A degree of polymerization of 600 to 1000 can be obtained in this process.<sup>(70)</sup> The polymers obtained have a tensile modulus of 4800 PSI. If chloral is initiated below the threshold temperature, a homogeneous gel is not obtained and polymers with poor mechanical strength are isolated.<sup>(70)</sup> Lithium tertiary butoxide is a good initiator and reacts

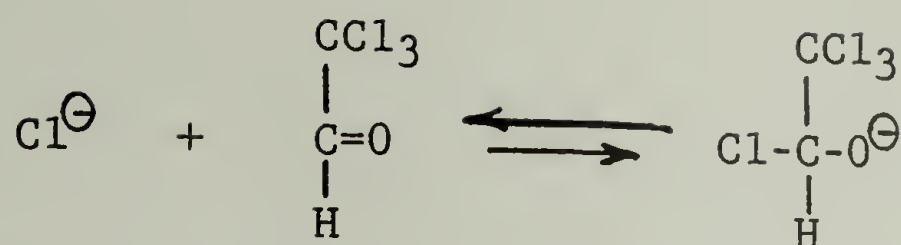
with one equivalent of chloral in a reversible equilibrium that is much further to the right according to an analysis by NMR.



One of the most effective initiators for cryotachensic polymerization is triphenylphosphine. Actually this phosphine is not the true initiator. It has been clearly established that the initiation reaction proceeds in two steps.<sup>(69)</sup> Firstly, a nearly instantaneous reaction of triphenylphosphine occurs with one mole of chloral to form triphenyldichlorovinylphosphonium chloride, a phosphonium salt.



(the structure of this salt has been thoroughly characterized) The chloride ion from this salt then initiates the polymerization



Initiation is reversible and the equilibrium is to the left. Cryotachensic polymerizations have been carried out in nonprotic inert solvents or in bulk. When a solvent, like methyl cyclohexane, was used highest conversions of 90% were obtained when the solvent concentration was about 10%.<sup>(68-69)</sup> All of these anionic polymerizations are sensitive to water and higher conversions were obtained with highly purified chloral when the polymerizations were conducted in dry equipment and under dry nitrogen. Unless moisture was excluded and unless initiation occurred above the ceiling temperature, intractable powders, brittle sheets, or small plugs of poor mechanical strength were obtained.

It has been possible to prepare chloral polymers for various measurements in the forms of films.<sup>(69)</sup> The polymer is insoluble in the monomer and in all solvents investigated when prepared by the cryotachensic method.<sup>(69)</sup> The polymer must be cast directly from the monomer.

## (2) Polymerization of Chloral with Acids

Chloral has been shown to polymerize in the presence of certain but not all acids. (1, 83-89) Protic acids such as  $\text{H}_2\text{SO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  and Lewis acids such as  $\text{AlCl}_3$  are effective initiators. These polymerizations usually are slower than the anionic polymerizations and the conversions are usually lower. (84, 95) Antimony pentahalides ( $\text{SbCl}_5$ ,  $\text{SbF}_5$ ) and aluminum chloride are special initiators for the polymerization of chloral. These two types of initiators caused the polymerization of chloral with nearly the same rate as in a typical anionic initiation. (84) Cationic initiators gave inhomogeneous polymers and a monomer casting technique is not operative.

## (3) Polymerization of Chloral with Organometallic Initiators

Chloral has been polymerized with various organometallic initiators. The system 2,6-dimethoxyphenyllithium-diethyl zinc, has been used to yield a polymer with a degree of polymerization of 600. (90, 91) Metal acetylacetonates and  $\text{Et}_3\text{Al}$  also induce the polymerization of chloral.



#### (4) Properties of Polychloral

##### Structure

Two types of chloral polymers were described in the early literature. The para polymer which is the cyclic trimer, and the meta polymers which are true linear polymers were reported. There was evidence quite early in the literature that the meta polymers were stereoregular substituted polyacetals. In 1959 a characterization study on polychloral samples (initiated with pyridine, with  $H_2SO_4$ ) was reported.<sup>(72)</sup> Infrared spectra revealed that metachloral is a substituted polyoxymethylene structure. The polymer, according to polarized infrared spectra, is not a planar zig-zag like polyoxymethylene but rather a helix with 3 or more repeat units per turn of the helix. Recent work<sup>(69)</sup> has indicated that polychloral in all cases examined was isotactic and helical with 4 monomer units per turn of the helix.

##### Crystallinity.

A recent study<sup>(72)</sup> also indicated that polychloral is semicrystalline by x-ray diffraction. Natta proved that crystalline polyaldehydes are stereoregular. The x-ray

diffraction spectra vary slightly from one polychloral sample to another. In some cases the diffraction lines were sharper for the polychloral samples prepared under anionic conditions than for the samples prepared with  $\text{H}_2\text{SO}_4$ .<sup>(72)</sup> The precise reasons for the differences in the x-ray diffraction spectra are not completely clear at this time. It was suggested<sup>(72)</sup> that those samples having sharper x-ray lines consisted of helices packed into larger regular crystalline units. The infrared spectra of all samples were identical however except in the C-H stretch region near  $2900\text{ cm}^{-1}$ , where slight differences were observed.<sup>(72)</sup> The carbon-oxygen and carbon-chlorine absorptions were identical which indicated that the same helical chain was obtained in all cases under cationic or anionic conditions.<sup>(72)</sup>

#### Stabilization and Degradation

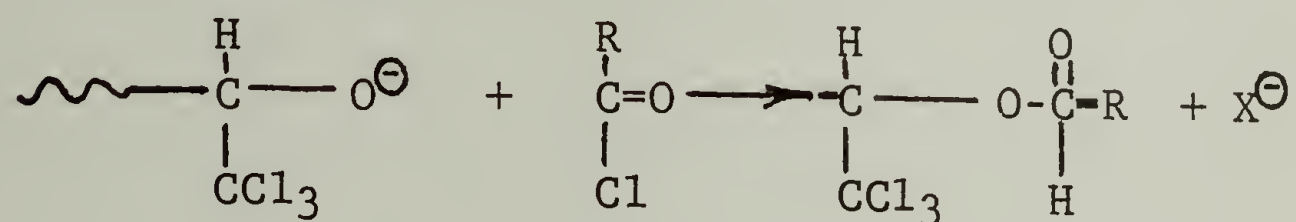
Thermal degradation has been found to be an excellent technique to characterize the chloral polymers with different end groups. The thermal degradation behavior of the polymers differed considerably depending on the end groups, the initiators used during polymerization, and the

purity of the reactants. Polymers prepared under anionic conditions degraded quantitatively to monomer above 140°C and no char remained.<sup>(93)</sup> The temperature of maxima rate of degradation of extracted polymers according to TGA analysis was higher for samples prepared with triphenyl phosphine than for samples prepared with tertiary amines,<sup>(93)</sup> or tetraalkylammonium chlorides.<sup>(93)</sup> It is believed that the differences in thermal stability are due to differences in end groups, molecular weights and crystallinities.<sup>(84, 93)</sup>

Polychloral prepared with initiation below the threshold temperature has been reported as being capable of stabilization by endcapping.<sup>(77)</sup> Polychloral was stabilized under acid conditions by treatment with acid chlorides or acid anhydrides. Evidence for endcapping was provided by infrared analysis. Stabilized polychlorals possessed good stability towards dimethyl formamide and adequate stability to temperatures about 200°C<sup>(76, 77)</sup>

Polychloral prepared with initiation above the threshold temperature, in cryotachensic polymerizations, could not be stabilized by treatment with acid chlorides

or acid anhydrides.<sup>(86)</sup> However a new method was developed to stabilize these polymers by introducing stable acyl end groups by carrying out an anionic cryotachensic polymerization in the presence of acid chlorides.<sup>(95)</sup> The acid chlorides caused chain termination to occur to give polychloral chains with ester end groups.

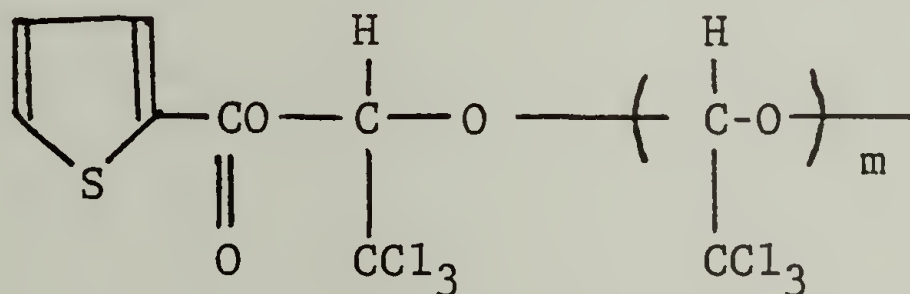


which could be identified in the infrared spectra. Analysis by DTG was found to be an excellent technique for the analysis of the extent of endcapping and the thermal stability of the chloral polymers.<sup>(93)</sup> The DTG for the decomposition of polychloral prepared in the presence of acetyl chloride with triphenyl phosphine as initiator showed two maxima which indicated that the polymer contained two fractions. The more stable fraction which had a maximum at 285°C contained ester end groups and represented 70 percent of the polymer. Phosphorous pentachloride in CCl<sub>4</sub> was also used successfully to stabilize chloral polymers.<sup>(68)</sup> After a 4 hour treatment in .



refluxing  $\text{PCl}_5/\text{CCl}_4$  solution chloral polymers were stable and had a maximum in the DTG curve at  $285^\circ\text{C}$ .

The chain termination technique was also used to estimate the minimum molecular weight of polychloral. (84, 93) The intensity of the ester carbonyl endgroup was compared to the intensity in standards consisting of polychloral-polymethylmethacrylate composites of known composition. The <sup>nu</sup>member average molecular weights were approximately 30,000 or a  $\text{Dp}_n$  of 200. The molecular weight was also estimated by carrying out the anionic polymerization with certain initiators which became permanently attached to the polymer chains. The concentration of the end groups was estimated by optical methods. One example is shown below.



and in this case the  $\text{Dp}_n$  reached 1,800. (70)

The thermal properties were characterized recently. (69) Chloral polymers showed neither a  $T_g$  nor a  $T_m$  below the

decomposition temperature according to analysis by DSC and torsional braid measurements.

b. Polydichloroacetaldehyde

Dichloroacetaldehyde polymers were first discovered in 1868 when it was observed that dichloroacetaldehyde was polymerized upon standing or in the presence of HCl.<sup>(3)</sup>

This polymer was insoluble and amorphous.

The monomer in a more recent study was distilled from H<sub>2</sub>SO<sub>4</sub>, condensed as a pure hydrate, distilled a second time from H<sub>2</sub>SO<sub>4</sub> passing the distillate vapor through a calcium chloride tube and this vapor was condensed to form a semi-crystalline polymer.<sup>(75)</sup> Dichloroacetaldehyde was polymerized to a higher molecular weight polymer with hydroxyl end groups with Lewis acid initiators. Anionic initiators which readily polymerize chloral were not effective for the polymerization of dichloroacetaldehyde.<sup>(78)</sup> The initiator BF<sub>3</sub>Et<sub>3</sub>O at 0°C produced a polydichloroacetaldehyde with a  $Dp_n$  of more than 400. This polymer could be stabilized by treatment with acetic anhydride to increase its thermal stability. The thermal stability was inferior to that of polychloral however. X-ray diffraction patterns

indicated that this polymer was amorphous. The polymer was soluble in tetrahydrofuran and methylethylketone.

c. Polychloroacetaldehyde

Chloroacetaldehyde polymerized spontaneously or in the presence of HCl when the polymer was isolated for the first time in 1882.<sup>(2)</sup> Chloroacetaldehyde also polymerized after it was distilled from concentrated  $\text{H}_2\text{SO}_4$  and was allowed to stand in a glass vessel at room temperature according to several reports.<sup>(60)</sup> The polymer obtained by this method was characterized recently by infrared spectroscopy and x-ray analysis. This polymer was found to be semi-crystalline. Chloroacetaldehyde has been polymerized with  $\text{Et}_2\text{Zn}$  in a yield of 19% to a highly crystalline polymer.<sup>(100)</sup>  $\text{BF}_3\text{Et}_2\text{O}$  produced a nearly 100% amorphous polymer in 38% yield.  $\text{AlEtCl}_2$  and  $\text{AlEt}_2\text{Cl}$  yielded polymers with about 50% crystallinity in 30% yield. It was also found that  $\text{BF}_3$  initiated the polymerization of chloroacetaldehyde at  $-10$  to  $-50^\circ \text{C}$  to an elastic amorphous thermoplastic.<sup>(101)</sup> The thermal stabilities of the polymers obtained from chloroacetaldehyde and  $\text{AlEt}_2\text{Cl}$  or  $\text{AlEtCl}_2$  were below the thermal stabilities of unstablized

polychloral prepared from chloral and  $\text{H}_2\text{SO}_4$ .<sup>(102)</sup> A sample of polydichloroacetaldehyde obtained by  $\text{BF}_3\text{Et}_2\text{O}$  initiation was of intermediate thermal stability.

## 2. Fluoroacetaldehyde Polymers

### A. Polyfluoral

Fluoral polymers were obtained first in 1950 without added initiator. The product obtained in this spontaneous polymerization was insoluble in common solvents.<sup>(102, 103)</sup>

Fluoral polymerizes rapidly in the presence of anions and Lewis bases at room temperature and lower temperatures. Alkali metal cyanides and halides, alkali metal carboxylates, sulfonium halides, quaternary ammonium halides, triarylphosphines and trialkylphosphites were suitable initiators.<sup>(104, 111)</sup> Amorphous, soluble, elastomeric presumably atactic polyfluoral has been prepared in non-polar diluents in the presence of cesium fluoride at  $-78^\circ\text{C}$ .<sup>(104)</sup>

This polymer was distinguished by its solubility in 2,2-bis-(trifluoromethyl)-1,3 dioxolanes, and by x-ray analysis. This polymer could be stabilized by treatment with  $\text{SF}_4$ . At  $40^\circ\text{C}$  however, fluoral polymerized in the



presence of cesium fluoride to give a white friable powder which was insoluble and infusible. This polymer was crystalline according to x-ray diffraction patterns.<sup>(104)</sup> The polymer solubility was directly related to the crystallinity.<sup>(104)</sup>

Fluoral may also be polymerized in the presence of certain acids. It was shown that anhydrous  $\text{PF}_5$  was a particularly effective initiator and produced rubbery amorphous polymers. This polymer had an inherent viscosity of 0.82 in 1,3-dioxolane and showed excellent thermal stability. Protic acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HCOOH}$  have been used as fluoral initiators but were not as effective as Lewis acids. The cationic initiators  $(\text{C}_6\text{H}_5)_3\text{CCl}$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ ,  $\text{AlCl}_3/\text{COCl}\cdot\text{CH}_3$ ,  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{C}_7\text{H}_7\text{SbCl}_6$  were also effective. The nature of the polymeric product was a function of the reaction conditions; either a crystalline solid or a soluble elastomer was obtained.<sup>(104)</sup> It has also been reported that  $\text{HCF}_2\text{SO}_3\text{H}$  and  $\text{HF}$  are not good initiators.<sup>(104)</sup>

A radical polymerization of fluoral with peroxides was claimed in 1954.<sup>(103)</sup> Further evidence for a radical

polymerization was reported when it was found that AIBN in the presence of ultraviolet radiation polymerized fluoral. (105-107) This polymerization ceased with the removal of the radiation source and benzoquinone or diphenylpicrylhydrazil were effective inhibitors. As further evidence of a radical mechanism  $C^{14}$  labelled AIBN was used and polymer endgroups contained initiator fragments. (105-110)

#### B. Polychlorodifluoroacetaldehyde

Chlorodifluoroacetaldehyde was reported to polymerize spontaneously on standing. (113) A more complete investigation of the polymerization of this monomer was reported recently. (114) The compounds  $Ph_3P$ ,  $Al(C_2H_5)_3$ ,  $Li^+O^-C(CH_3)_3$ ,  $SbCl_5$  and  $H_2SO_4$  were effective initiators. The solubility properties of these polymers depended on the reaction conditions. In some cases acetone soluble fractions were isolated. (113)

#### C. Polydichlorofluoroacetaldehyde

The previously unknown dichlorofluoroacetaldehyde was synthesized and polymerized recently. (115) The compounds

$\text{Ph}_3\text{P}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{TiCl}_4$ ,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{SbCl}_5$ , and  $\text{LiOC}(\text{CH}_3)_3$  were effective initiators. The thermal degradation behavior depended on the initiator and reaction conditions for these polymers. The polymers could be stabilized by treatment with acetic anhydride.

#### D. Polydifluoroacetaldehyde

Difluoroacetaldehyde has been reported to polymerize at  $-80^\circ\text{C}$  in the presence of triethylphosphite.<sup>(111)</sup> The polymer could be stabilized by the treatment with  $\text{PCl}_5$  in  $\text{CCl}_4$ .

### 3. Other Fully Halogenated Acetaldehydes

One old report exists of a 'polymer' obtained from dichlorobromoacetaldehyde and  $\text{H}_2\text{SO}_4$ .<sup>(65)</sup> The structure of this product was not characterized and its existence has never been confirmed. Chlorodibromoacetaldehyde, bromal, difluorobromoacetaldehyde, dibromofluoroacetaldehyde, and bromochlorofluoroacetaldehyde polymers have never been reported.

### 4. Other Partially Halogenated Acetaldehydes

Dibromoacetaldehyde has been reported to polymerize

to give an amorphous solid.

#### D. Haloacetaldehyde Copolymers

##### 1. Chloral Copolymers

##### A. Aldehyde Copolymers

Chloral has been shown to copolymerize with dichloroacetaldehyde with zinc alkyl initiators and diethylcadmium at temperatures below  $-40^{\circ}\text{C}$  in toluene to high molecular weight copolymers. Copolymers with substantial amounts of dichloroacetaldehyde were insoluble and infusible. These copolymers were prepared by a monomer casting technique as films and sheets. The initiator was added below the ceiling temperature and coherent sheets could be obtained only for the chloroaldehyde-dichloroacetaldehyde copolymers and not for chloral homopolymers in this study. (80, 97)

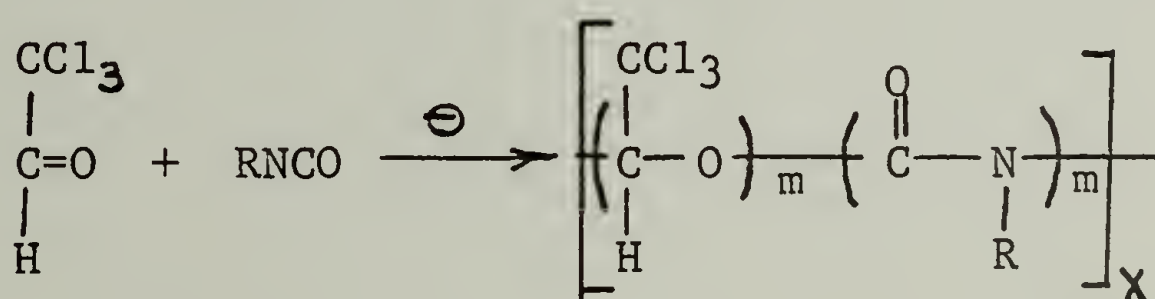
Chloral has also been copolymerized under anionic conditions with fluoral. (68) Chloral was shown to copolymerize with formaldehyde at low temperatures. Triphenylphosphine, trialkylamines and triethylaluminum yields copolymers with a wide range of compositions and many fractions. (134-136) Recently a polymer of propionaldehyde



and chloral has been claimed but this has not been verified yet.

## B. Isocyanate Copolymers

Copolymerization of chloral with isocyanates particularly phenylisocyanate and p-chlorophenyl-isocyanate was described in 1965. (97, 116) Since that time many patents have appeared which claim chloral isocyanate copolymers with improved thermal stabilities. (116-124) Chloral and aryl or alkyl isocyanates were shown to copolymerize under anionic conditions to yield soluble and fusible products of insoluble and infusable products depending on the specific isocyanate and its proportion in the feed.



Initiators suitable for anionic chloral homopolymerizations were also suitable for the chloral isocyanate copolymerizations. The cryotachensic technique was used to give tough copolymers of a predetermined shape with excellent thermal stabilities. Copolymers made by this method

containing from about 80 to 90 mol. percent chloral and 20 to 10 mol percent isocyanate were insoluble in common organic solvents. (115-119) They were also infusible at temperatures up to their decomposition point. Copolymer films showed greater clarity than the homopolychloral films and this increase in clarity was attributed to decreased crystallinity in the copolymer. These copolymerizations were nearly bulk polymerization with a low concentration of a diluent like toluene or methyl cyclohexane present or were true bulk copolymerizations.

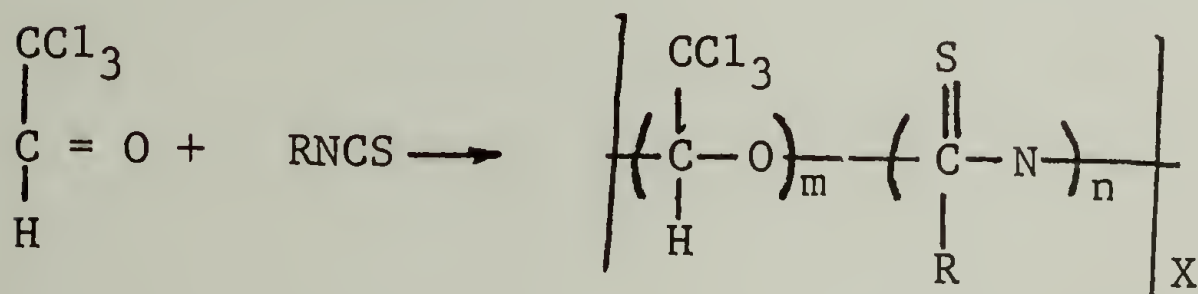
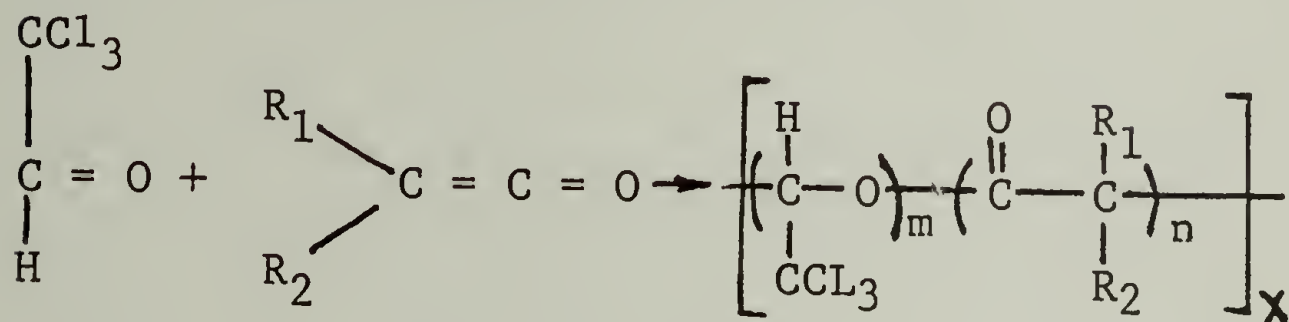
The copolymerization of chloral with phenyl isocyanate and with n-butyl isocyanate in solution was reported in 1971. Chloral was copolymerized in several solvents with phenyl isocyanate and several initiators were used. (125) The solubility of the copolymers in  $\text{CHCl}_3$  was determined by both the initiator and the solvent. If phenyl isocyanate was copolymerized with KCN in DMF at  $-78^\circ\text{C}$  a copolymer was formed in  $\text{CHCl}_3$  and having a  $T_m$  of  $230^\circ\text{C}$ . This copolymer contained 60% chloral according to analysis for N. Another copolymer of chloral and phenyl isocyanate of the same composition was prepared by n-butyl lithium in

ether but this copolymer was insoluble in  $\text{CHCl}_3$ . A third copolymer with this composition was prepared in benzene with triethyl amine.<sup>(125, 126)</sup> It was concluded that this insoluble copolymer was more crystalline and that this crystallinity was due to the proximity of the  $\text{Li}^\oplus$  counterion to the propagating center. This proximity caused an orientation effect on the entering monomers resulting in a more crystalline polymer.<sup>(126)</sup> The relative reactivities of chloral and phenyl isocyanate in hexane and in ether with butyl lithium initiations were determined. The reactivity ratios at low conversion were reported to be  $r_1$  (chloral) = 1.2,  $r_2$  (phenylisocyanate) = 0 in hexane and  $r_1 = 0.5$ ,  $r_2 = 0$  in ether at  $-78^\circ\text{C}$ . The authors concluded that the reactivity of chloral increased as the tightness of the ion pair. They also showed that phenyl isocyanate was more reactive than butyl isocyanate in chloral copolymerizations.<sup>(126)</sup>

#### Ketene and Isothiocyanate Copolymers

Chloral was shown to copolymerize to greater than 80% conversion with isothiocyanates.<sup>(127-133)</sup> The cryotachensic

polymerization technique was employed to produce coherent shape objects composed of chloral ketene copolymers or chloral isothiocyanate copolymers.



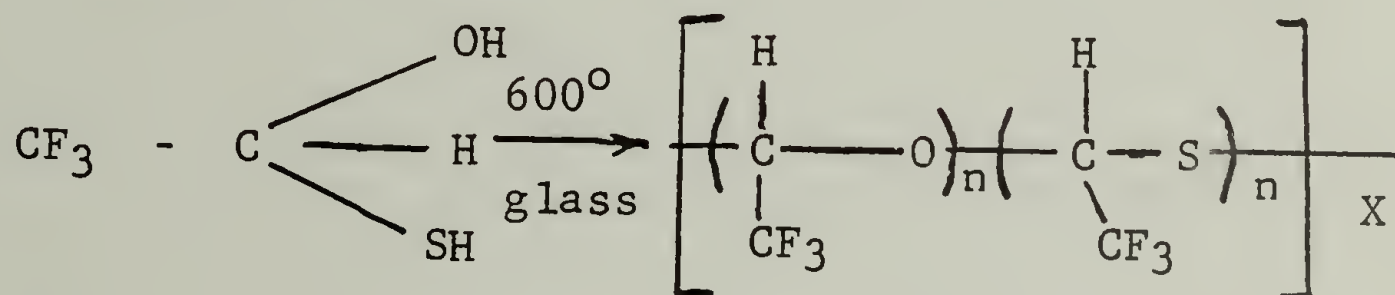
The initiators used for anionic homopolymerizations of chloral or for chloral isocyanate copolymerizations were effective for the chloral ketene and chloral isothiocyanate copolymerizations.

Several other copolymers of chloral have been claimed but not verified. A number of patents have claimed copolymers of chloral and formaldehyde<sup>(134-136)</sup> ethylene oxide,<sup>(137)</sup> trioxane<sup>(138, 139, 140)</sup> propionaldehyde<sup>(145)</sup> vinyl acetate,<sup>(138, 139)</sup> 3,3'-dichloromethyl oxetane<sup>(138, 139)</sup> acetaldehyde<sup>(145)</sup> and 1,3-dioxolane.<sup>(138, 139)</sup>



## 2. Fluoral Copolymers

A copolymer of fluoral and formaldehyde has been claimed.<sup>(142)</sup> Polymerizations were carried out in toluene or cyclohexane and were initiated by quaternary ammonium acetates. The polymers could be stabilized by treatment with acetic anhydride. A copolymer of fluoral with ethylene in a radical polymerization has been claimed.<sup>(143)</sup> This copolymer had an inherent viscosity of 0.57. It has also been shown that fluoral will copolymerize with acrylonitrile.<sup>(144)</sup> In addition a fluoral-thiofluoral copolymer has been reported.<sup>(145)</sup> A perfluorinated olthiol was pyrolyzed over glass at 600°C and the products copolymerized in a cold trap to a 82/18 trifluorothioaldehyde/fluoral copolymer.<sup>(146)</sup>



## C. Bromal Copolymers

Two recent patents claimed that bromal could be copolymerized with acetaldehyde and with isobutyraldehyde.<sup>(146)</sup> No homopolymers of bromal were reported.

## EXPERIMENTAL PART

## II. EXPERIMENTAL PART

## A. CHEMICALS

Chemicals and reagents were obtained from the following sources:

1. Reagents

Acetic anhydride	E
Acetyl chloride	E
Acrylonitrile	A
Aluminum Tribromide	F
Aluminum Trichloride	F
Antimony Pentachloride	F
Antimony Trifluoride	Allied
Azobisisobutyronitrile	E
Boron trifluoride	MT
Bromal	A
Bromine	F
N-Bromosuccinimide	E
M-butylisocyanate	A
Cesium bromide	Al
Cesium chloride	Al
Cesium fluoride	Al

Cesium Iodide	A1
Calcium Carbonate	Ma11.
✓Chloroacetaldehydediethylacetal	A
Chloral	DS
Collidine	A
1,2-Dibromoethane	E
Dichloroacetaldehydediethylacetal	A
Dichloroacetylchloride	E
Dimethyl Sulfoxide	A
Dioxolane	
Epichlorohydrin	E
Hexamethylphosphoramide	E
Lithium Bromide	F
Lithium Chloride	F
Lithium tertiary butoxide	V
p-Methylphenylisocyanate	A
Molecular Sieves	MCB
Phenylacetaldehyde	A
Phenylisocyanate	A
Pivalolactone	E
Poly (oxyethylene) (4000)	U C



Potassium Fluoride	MCB
Pyridine	E
Quinoline	E
Sebaryl chloride	A
Sodium tetraphenylborate	B
p-Cl-styrene	A
Sulfuric acid	F
Tetrahydrofuran	M
Titanium Tetrachloride	Al
Toluene	M
Tri-n-butylamine	E
Tri-n-butylphosphine	A
Trichloroacetyl chloride	E
Triethyl aluminum	V
Triethylamine	E
Triethylphosphite	A
Trifluoromethane sulfonic acid	A
Triphenylamine	E
Triphenylphosphine	A
p-xylene	F

2. Solvents

Acetone	F
Benzene	F
Chloroform	F
o-Dichlorobenzine	A
Diethyleneglycoldimethylether	A
Dioxane (spectral	MCB
Ether	F
Hexane	F
Methyline chloride	F
Nitrobenzene	E
Nitromethane	E

3. Sources

A = Aldrich Chemical Company

Al = Alfa Inorganics

Allied = Allied Chemical Company

B = J. T. Baker

DS = Diamond Shamrock Corporation

✓ E = Eastman Kodak

F = Fischer Scientific Co.

GE = General Electric

M = Mallinckrodt Chemical Co.

MCB = Matheson, Coleman & Bell

MT = Mathison Gas Products

P = Polysciences, Inc.

UC = Union Carbide Corporation

V = Ventron Inorganics

#### B. Purification of Solvents and Reagents.

All of the distillations, except for the distillation of chloral were done in a distillation apparatus equipped with a 30 cm. Vigreux column. Distillations which were carried out under reduced pressure were done with magnetic stirring and a Claisen head. In some cases shredded isotactic polypropylene was used to prevent bumping. The pressure was stabilized with a manostat.

Chloral (obtained from the Diamond Shamrock Company) was allowed to reflux over powdered phosphorous pentoxide (for 1 liter of chloral about 50 gms. of phosphorous pentoxide) for 24 hours in a dry nitrogen atmosphere.<sup>(93)</sup> Chloral was then transferred into a carefully dried distillation apparatus which consisted of a 100 cm. long

tetrachloride ( $136.4^{\circ}\text{C}/760\text{ mm}$ ) were distilled through a 30 cm. Vigreux column under dry helium. A shorter column was not satisfactory.

Acrylonitrile was purified by passing it through a column of silica gel under a slight nitrogen pressure and was used immediately.

Aluminum tribromide and aluminum trichloride were used from freshly opened bottles and were handled in a nitrogen filled dry box.

Azobisisobutyronitrile was recrystallized three times from dry methanol and dried at 0.1 mm for 16 hours at  $25^{\circ}\text{C}$ .

N-bromosuccinimide was recrystallized from water (50 g. in 500 ml.), filtered, washed with water, air dried on the filter, and then dried at  $60^{\circ}\text{C}$  in a vacuum over (1 m.m.) for 16 hours. The white plates were ground into a very fine powder with a mortar and pestle.

Cesium bromide, cesium chloride, cesium bromide, and cesium iodide were used from freshly opened bottles (packaged under argon). Solutions of these salts were prepared in a glove bag filled with dry nitrogen.

Chloroacetaldehydediethylacetal, di chloroacetaldehydediethylacetal, and epichlorohydrin were stored over



molecular sieves (3A) for 1 week prior to use.

Dimethyl sulfoxide was distilled from calcium hydride at reduced pressure ( $60^{\circ}\text{C}/8\text{ mm}$ ) and stored over molecular sieves (3A).

Lithium bromide, lithium chloride, and potassium fluoride, were dried at  $180^{\circ}\text{C}$  at  $0.1\text{ mm}$ . for 16 hours in the presence of phosphorous pentoxide, in a drying pistol.

Styrene ( $40^{\circ}\text{C}/15\text{ mm}$ ) and p-chlorostyrene ( $66^{\circ}\text{C}/10\text{ mm}$ ) were distilled from calcium hydride under nitrogen at reduced pressure and were used immediately.

Tetrahydrofuran was distilled ( $78^{\circ}\text{C}/760\text{ mm}$ ) from lithium aluminum hydride under dry nitrogen just prior to use.

Triphenyl amine was recrystallized from spectral grade methanol (15 g in 125 ml.) collected on a filter, washed with cold benzene, and dried in a stream of dry nitrogen.

Benezene, cyclohexane, n-hexane, methyl cyclohexane, toluene and xylene were distilled from calcium hydride under nitrogen in a distillation head at a reflux ratio of 20 to 1. Dichloromethane and chloroform were distilled

from powdered phosphorous pentoxide (20 g/2 liters) and were stored in a column filled with molecular sieves (3A).

Nitrobenzene was steam distilled after the addition of dilute sulphuric acid. The distillate was separated, dried over calcium chloride, and distilled under nitrogen (90°C/ 20 mm). O-dichlorobenzene was dried over calcium chloride and distilled under nitrogen (90°C/ 20 mm).

Solvents and reagents sensitive to water or oxygen were stored under nitrogen in specially prepared tubes.

### C. MEASUREMENTS

Infrared spectra was obtained on a Perkin Elmer 727 Infrared Spectrometer ( $5000\text{-}600\text{ cm}^{-1}$ ) at a "normal" scan rate or on a Beckman Infrared Spectrometer ( $4000\text{-}250\text{ cm}^{-1}$ ) at a slow scan rate. The potassium bromide and thallous bromide used for the preparation of the pellets were dried at  $180^{\circ}\text{C}$  at a pressure of 1 mm. of  $\text{Hg}$  in a drying pistol over phosphorous pentoxide. The polystyrene band at  $1601\text{ cm}^{-1}$  was used as the standard and was recorded on each spectrum.

Nuclear magnetic resonance spectras (PMR) were obtained on a Hitachi-Perkin Elmer R-24 Spectrometer or on a 90  $\text{MHz}$  Perkin Elmer R-24 Spectrometer with TMS or chloroform as the internal standard.  $\text{C}^{13}$  NMR spectra were obtained on a Bruker 90 M  $\text{H}_2$  Spectrometer.

DSC measurements were made under nitrogen on a Perkin Elmer DSC - 1B, with a UUI Temperature Program Control. The scan rate was  $20^{\circ}\text{C}/\text{minute}$ . The instrument was calibrated against benzoic acid (m.p.  $122^{\circ}\text{C}$ ) and salicyclic acid (m.p.  $159^{\circ}\text{C}$ ). For low temperature scans the instrument was

calibrated against cyclohexane (m.p. 5°C) and nitrotoluene (m.p. 52°C).

TGA data were obtained on a Perkin Elmer TGA-1 Thermobalance under nitrogen at a heating rate of 20°C/minute.

The heating rate was regulated by a Perkin Elmer UU1 Temperature Program Control.

Gas chromatograms of the monomers were obtained on a Varian Associates Model 920 gas chromatograph on a 2 meter column packed with 35% Diisodecyl Phthalate or Chromosorb W/ or on a 1 meter Poropak Q column.



D. BROMODICHLOROACETALDEHYDE SYNTHESIS AND  
POLYMERIZATION

1. Synthesis of Bromodichloroacetaldehyde from Chloral

To a dried 3 neck 1000 ml. flask was added triphenyl phosphine (90.0 g, 0.67 mole) in dry dichloromethane (200 ml) from a dropping funnel under a nitrogen blanket. The flask was cooled at 0°C in an ice bath for 10 minutes. Freshly distilled chloral (33 ml, 0.33 mole) in dichloromethane (50 ml) was added to the funnel with a dry syringe. The solution was stirred at a rapid rate without any splashing and the chloral solution was added dropwise over a 30 minute period and clear solution was stirred for an additional 30 minutes. Bromine (10 ml, 0.33 mole) in dichloromethane (25 ml) was added dropwise at a rate that allowed the red color to vanish. Addition was complete after 5 hours and during the addition of the last 3 ml of bromine solution the solution remained light orange. The solution was stirred under the nitrogen blanket for 2 additional hours and the flask was then set up for a distillation. The flask was equipped with a condenser, a thermometer, a still head and a nitrogen inlet tube to

remove dichloromethane using an oil bath at  $50^{\circ}\text{C}$  while passing a slow nitrogen stream through the nitrogen inlet tube into the receiver.

The 3 neck flask was then equipped again with an addition funnel, a reflux condenser and a nitrogen inlet tube. Dioxane was added (75 ml) and the phosphonium salt was broken up by stirring. Water (6.5 ml) in dioxane (75 ml) was added dropwise over a one hour period at  $25^{\circ}\text{C}$  under the blanket of nitrogen. The partially hydrolyzed salt was allowed to stand in the wet dioxane for 2 hours and then the mixture was stirred and heated at  $80^{\circ}\text{C}$  for one hour while a slow nitrogen stream was passed over the surface to allow the HBr and HCl to escape through the condenser.

The flask was allowed to cool at  $25^{\circ}\text{C}$  and then it was equipped with an adapter connected to a condenser and with 2 stoppers in the other 2 necks; a receiving flask was attached to the condenser with a vacuum adapter and was cooled in a dry ice isopropyl alcohol bath. The 3-neck flask was heated with an oil bath and the volatile contents in the flask were distilled at 15 mm pressure. The solution was stirred rapidly but without splashing and the oil

bath was gradually heated from 25°C to 70°C. Dioxane, aldehyde, and aldehyde hydrate were collected. The stirring was maintained as long as possible so that the residue did not trap the aldehyde.

The distillate was transferred to a 500 ml 3-neck flask which was equipped with a reflux condenser, a nitrogen inlet tube, and a stopper. The flask was purged with nitrogen and the mixture was brought to reflux with an oil bath for 10 minutes while a slow stream of nitrogen was passed over the surface. The flask was allowed to cool to room temperature and powdered phosphorous pentoxide (10.0 g) was added. It was then connected to a distillation head and the reflux condenser was removed. The dioxane-aldehyde mixture was heated with an oil bath to 120°C and distilled into a 2-neck flask with a serum cap which was cooled in a dry ice-isopropyl alcohol bath under a blanket of nitrogen. The distillation removed most of the dioxane at 120°C and very little of the aldehyde (b.p. 127°C) distilled. The distillate composition was monitored by gas chromatography during the distillation (Diisodecyl phthalate 36% on chromosorb W). The distillation was continued until



aldehyde appeared in the distillate. The receiver flask was now replaced and the liquid remaining in the 3-neck flask was distilled at 200 mm pressure at 120°C. The aldehyde and dioxane mixture collected was stored in a sealed flask overnight in the dark.

A gas chromatogram of this fraction was taken to determine the percent dioxane in the sample. The fraction was then transferred to a 100 ml round bottom flask equipped with a capillary nitrogen inlet and a 19/32 standard taper joint. The flask was then attached to a laboratory size spinning band column, flask and column were purged with nitrogen and the flask was heated with an oil bath to 120°C with spinning. Dioxane distilled first, the receiver was replaced and the distillation was continued at 100 mm pressure and 110°C until 24 ml had been collected. This second fraction was transferred to a dry 100 ml round bottom flask containing 3.0 g of powdered  $P_2O_5$ , it was purged with dry nitrogen and connected to a Vigreux distillation column. The apparatus was wrapped with aluminum foil to protect the aldehyde from light during distillation. The flask was heated with an oil bath to 140°C and the



distillation was carried out at 760 mm pressure. The first 6 ml of the distillate was red and was collected. The receiving flask was replaced and 18 ml was collected as a middle cut.

Bromodichloroacetaldehyde (18 ml, 60% yield) was obtained as a colorless liquid with an irritating odor. The infrared spectrum (neat) showed absorptions at  $1754\text{ cm}^{-1}$  (s) (C=O stretching),  $3508\text{ cm}^{-1}$  (overtone of stretching),  $2855\text{ cm}^{-1}$  (m) (C-H stretch, aldehyde),  $1357\text{ cm}^{-1}$  (s) (C-H bend),  $1022\text{ cm}^{-1}$  (s),  $983\text{ cm}^{-1}$  (s) (C-C stretch),  $840\text{ cm}^{-1}$  (vs) (C-Cl stretch) and  $682\text{ cm}^{-1}$  (vs) (C-Br stretch). The PMR spectrum showed a singlet at  $\delta = 8.9$  (TMS). This aldehyde had a boiling point of  $127-128^{\circ}\text{C}$  at 760 mm, and a density of 1.90 at  $25^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_2\text{HBrCl}_2\text{O}$ : C, 12.52%, H, 0.53%; Cl, 36.96%; Br, 41.65%. Found: C, 12.24%; H, 0.66%; Cl, 36.72%; Br, 41.34%.

In a second experiment bromodichloroacetaldehyde was obtained in 46% yield. If the hydrolysis of the phosphonium salt was done in dichloromethane instead of dioxane the hydrolysis was not complete and very little aldehyde was isolated. If ether was used as the solvent in the

hydrolysis step the workup afterward was difficult because the triphenylphosphine oxide oxide formed a gum and the aldehyde could not be distilled out efficiently. If the bromine was added too rapidly a side reaction took place and little aldehyde was isolated after hydrolysis. The apparatus, the dichloromethane and triphenylphosphine had to be very dry for the first step, the reaction of triphenylphosphine with chloral, to be successful. If any moisture was present a gum formed and the experiment had to be started again. In several experiments dry ether was used as the solvent for the chloral-triphenylphosphine reaction. A 5% quantity of insoluble white gum formed during addition of the chloral in this solvent.

The use of dichloromethane in the solvent for the chloral/ $\text{Ph}_3\text{P}$  reaction obviated this problem and the salt in this solvent was less susceptible to attack by adventitious water.

2. Preparation of Bromodichloroacetaldehyde from Dichloroacetaldehyde diethyl acetal

A 500 ml 3-neck round bottom flask was equipped with a pressure equalizing addition funnel, a nitrogen inlet tube,

liquid was poured into a separatory funnel containing cold concentrated sulphuric acid (200 ml). The separatory funnel was shaken for one minute and this allowed to stand at room temperature for 30 minutes. Two layers separated after a few minutes, the bottom layer (aldehyde) was collected in a 250 ml Erlenmeyer flask containing calcium carbonate (10 g).

A dried 100 ml round bottom flask was purged with dry nitrogen, powdered phosphorous pentoxide (5.0 g) was added and the aldehyde was filtered from the calcium carbonate through a fritted funnel under nitrogen pressure into the flask. A dried distillation head was placed on the 100 ml flask in place of the funnel. The apparatus was lowered into an oil bath and the liquid was then distilled at 127°C at 760 mm. 5 ml of aldehyde were collected, the receiving flasks changed, and the next 30 ml were collected. The distillation was repeated, from phosphorous pentoxide (3.0 g). The first 2-3 ml were red and were discarded. The next 28 ml of colorless liquid were collected. Bromodichloroacetaldehyde was obtained (27 ml, 50.1 g, 28% overall yield) as a colorless liquid with an irritating odor.



The infrared spectrum was superimposed on the spectrum for bromodichloroacetaldehyde obtained from chloral and triphenylphosphine.

3. Attempted Preparation of Bromodichloroacetaldehyde from Dichloroacetylchloride Bromine and Red Phosphorous.

A dried 250 ml neck round bottom flask was dried for 72 hours at 120°C, and fitted with a nitrogen inlet tube. The flask was purged with dry nitrogen and was equipped with a reflux condenser and a stirring bar. Dichloroacetyl chloride (74 g, 0.5 mole) and red phosphorous (1.0 g, 0.032 mole) were placed in the flask and was inserted into an oil bath at a temperature of 105°C. Bromine (30 ml, 0.5 mole) was added dropwise from the addition funnel while the solution was stirred. The temperature in the bath was then raised to 110°C and a very gentle reflux of the dichloroacetyl chloride was maintained. The red color was not discharged and no hydrogen bromide was evolved. The bromine was added over a 6 hour period to the solution under the nitrogen blanket. At the end of this time the solution was very dark red. The flask was heated at a gentle reflux for



9 more hours and then was allowed to cool to room temperature. A gas chromatogram of the flask contents (Poropak Q, 90°) contained only one major peak corresponding to the starting material dichloroacetyl chloride.

4. Attempted Synthesis of Bromodichloroacetaldehyde from Chloral and Lithium Bromide.

A dried 3 neck 250 ml round bottom flask was equipped with a nitrogen inlet tube, a reflux condenser and a ground glass stopper. The flask was allowed to cool to room temperature and the stopper was removed. Chloral (50 ml, 0.5 mole) and anhydrous lithium bromide (43.4 g, 0.5 mole) a 1-1/2" stirring bar were placed in the flask. The mixture was heated with stirring at reflux for 12 hours. The flask was allowed to cool and a gas chromatogram of the product was taken (Poropak Q). The chromatogram indicated the presence of almost pure chloral. During the reaction almost none of the lithium bromide went into solution.

5. Attempted Preparation of Methylbromodichloroacetate from Methyldichloroacetate, Bromine and Benzoyl Peroxide.

A dried 3 neck 250 ml round bottom flask was equipped

with a nitrogen inlet tube, a water-cooled reflux condenser, and a ground glass stopper. The flask was allowed to cool to room temperature and the stopper was removed.

Methyl dichloroacetate (75 ml), bromine (25 ml), benzoyl peroxide (2.0 g) and a 3/4" stirring bar were placed in the flask. The mixture was brought to reflux with an oil bath for 12 hours under the nitrogen blanket and then was allowed to cool to room temperature. A PMR spectrum of the flask contents was identical to the PMR spectrum (3 to 1 ratio) of methyldichloroacetate.

6. Attempted Preparation of Methyl Bromodichloroacetate from Methyldichloroacetate, Bromine and Potassium Persulfate.

A dried 3 neck 250 ml round bottom flask was equipped with a nitrogen inlet tube, a water-cooled reflux condenser, and a ground glass stopper. Methyldichloroacetate (75 ml), bromine (25 ml), potassium persulfate (3.0 g) and a 3/4" stirring bar were placed in the flask and the mixture brought to a reflux with an oil bath for 12 hours, and then was allowed to cool to room temperature. A PMR spectrum of the flask contents was identical to the PMR spectrum of the methyldichloroacetate.

7. Attempted Preparation of Methyl Bromodichloroacetate from Methyldichloroacetate and N-bromosuccinimide.

A dried 3 neck 500 ml round bottom flask was equipped with a nitrogen inlet tube, a reflux condenser, and a ground glass stopper. Methyl dichloroacetate (143 g, 1 mole) and N-bromosuccinimide (78 g, 0.5 mole) were placed in the flask and the mixture was heated at reflux for 12 hours under the nitrogen blanket and then allowed to cool to room temperature. The mixture was filtered through a 600 ml (10-15 u) fritted funnel; solid material was collected on the filter. The filtrate was then placed in a clean 500 ml round bottom flask and was distilled at 50°C at 10 mm pressure. A small quantity of solid material remained in the distilling flask. A PMR spectrum of the distillate was identical to the PMR spectrum of the starting material, methyl Dichloroacetate (128 g, 90%).

8. 2,4-Dinitrophenylhydrazone of Bromodichloroacetaldehyde.

To a 50 ml Erlenmeyer Flask were placed 2,4-dinitrophenylhydrazine (1.0 g), dry dimethyl formamide (5.0 ml), concentrated  $\text{H}_2\text{SO}_4$  (0.1 ml) and bromodichloroacetaldehyde



(0.25 ml, 2.5 mole). The flask was stoppered, the solution was shaken thoroughly and was allowed to stand at 0°C for 20 minutes. The color of the solution changed to a darker red after 2 minutes. Methanol was then added dropwise and the flask was agitated after each addition until a cloudiness appeared and then the flask was stoppered and allowed to stand at 0°C for one hour. An orange solid precipitated and was collected.

Methanol (10 ml) was added to the filtrate and the flask was stoppered and kept at 0°C for 2 hours. A light yellow-orange precipitated which was collected by filtration washed with cold methanol, and dried. The 2,4-dinitrophenylhydrazone of bromodichloroacetaldehyde was obtained as a light orange crystalline solid (m.p. 150°C).

An infrared specimen showed absorptions at: 3295  $\text{cm}^{-1}$  (m), 3070  $\text{cm}^{-1}$  (w), 3000  $\text{cm}^{-1}$  (vs), 1600  $\text{cm}^{-1}$  (vs), 1580  $\text{cm}^{-1}$  (vs), 1493  $\text{cm}^{-1}$  (s), 1412  $\text{cm}^{-1}$  (m), 1320  $\text{cm}^{-1}$  (vs), 1305  $\text{cm}^{-1}$  (vs), 1277  $\text{cm}^{-1}$  (vs), 1250  $\text{cm}^{-1}$  (m), 1216  $\text{cm}^{-1}$  (m), 1123-1106  $\text{cm}^{-1}$  (w), 1089  $\text{cm}^{-1}$  (s), 1055  $\text{cm}^{-1}$  (m), 918  $\text{cm}^{-1}$  (m), 838  $\text{cm}^{-1}$  (m), 820  $\text{cm}^{-1}$  (w), 759  $\text{cm}^{-1}$  (w), 740  $\text{cm}^{-1}$  (m), 723  $\text{cm}^{-1}$  (m). Anal. calcd. for  $\text{C}_8\text{H}_5\text{N}_4\text{O}_4\text{Cl}_2\text{Br}$ : N,



14.79%; H, 1.71%, C, 25.90%. Found: N, 14.91%, H, 1.40; C, 25.62.

9. Polymerization of Bromodichloroacetaldehyde with  $H_2SO_4$ .

A 12 in long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9. Freshly distilled bromodichloroacetaldehyde (4.0 ml, 40 mole) was added with a dry syringe (12" needle). Concentrated (98%) sulphuric acid (0.05 ml, 0.4 mole, 1 mol %) was added with a 50 ul syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then transferred to a refrigerator maintained at  $-10^{\circ}C$ . The tube was shaken thoroughly and was then left undisturbed for 7 days at  $-10^{\circ}C$ . During the first 6 hours little change was observed but after 24 hours a considerable quantity of white material appeared as a precipitate nearly filling the total volume of the liquid and at the end of one week a solid porcellan product was obtained.

The tube was warmed to room temperature and was then cut into sections about 1 inch long with a glass file. The friable polymer was removed and then soaked in ethanol (30

ml) and acetone (20 ml) for 24 hours in a glass stoppered Erlenmeyer flask. The insoluble product was collected on a medium (10-15 u) fritted funnel and the filtrate was saved and set aside. The product was soaked in acetone (20 ml) for 48 hours at 25°C, and filtered again and dried in a stream of nitrogen for 30 minutes. The filtrate was combined with the previous filtrate. The polymer was then dried in the presence of  $P_2O_5$  in an Abderhalden apparatus at 0.1 mm pressure for 16 hours to remove the solvent. Polydichlorobromoacetaldehyde (1.19 g, 31% yield) was obtained as a white powder. The infrared spectrum (KBr) showed absorptions at 3200-3400  $\text{cm}^{-1}$  (b, vw) (O-H stretch); 2944  $\text{cm}^{-1}$  (C-H stretch); 1370  $\text{cm}^{-1}$  (w); 1350  $\text{cm}^{-1}$  (m), 1311  $\text{cm}^{-1}$  (C-H bend); 1109  $\text{cm}^{-1}$  (vs), 1068  $\text{cm}^{-1}$  (vs), 1052  $\text{cm}^{-1}$  (vs), 949  $\text{cm}^{-1}$  (vs) (C-O stretches); 810  $\text{cm}^{-1}$  (C-C stretch); 789  $\text{cm}^{-1}$  (s), 753  $\text{cm}^{-1}$  (s) (C-Cl stretches); 664  $\text{cm}^{-1}$  (s) (C-Br stretch), 557  $\text{cm}^{-1}$  (m). Anal. Calcd. for  $C_2HBrCl_2O$ ; C, 12.52; H, 0.53; Br, 41.65; Cl, 36.96. Found: C, 12.90; H, 0.69; Br, 41.34; Cl, 36.72.

The combined filtrates from procedure 1 were evaporated to half volume in a stream of nitrogen and then poured

into n-hexane (50 ml). A white precipitate separated out and was collected on a medium (10-15 u) fritted funnel. The product was dried on the funnel in a stream of nitrogen and then dried in a desiccator for 16 hours at 15 mm pressure. The acetone soluble polybromodichloroacetaldehyde was obtained (0.213 g, 5.6%) as a light buff powder. The infrared spectrum (KBr) showed absorptions at 3200-3550  $\text{cm}^{-1}$  (b, m) (OH stretch); 2944  $\text{cm}^{-1}$  (m) (C-H stretch); 1370  $\text{cm}^{-1}$  (w); 1350  $\text{cm}^{-1}$  (m); 1311  $\text{cm}^{-1}$  (s) (C-H bend); 1109  $\text{cm}^{-1}$  (vs), 1068  $\text{cm}^{-1}$  (vs), 1952  $\text{cm}^{-1}$  (vs), 949  $\text{cm}^{-1}$  (vs) (C-O stretch); 810  $\text{cm}^{-1}$  (s) (C-C stretch); 789  $\text{cm}^{-1}$  (s); 753  $\text{cm}^{-1}$  (s) (C-Cl stretch); 664  $\text{cm}^{-1}$  (s) (C-Br stretch); 557  $\text{cm}^{-1}$  (m). Anal: Calcd. for  $\text{C}_2\text{HBrCl}_2\text{O}$ : C, 12.52%; H, 0.53%; Br, 41.65%; Cl, 36.96%. Found: C, 12.24%; H, 0.66%; Br, 41.27%; Cl, 36.69%.

10. Polymerization of Bromodichloroacetaldehyde with Sb Cl<sub>5</sub>.

A 12 inch long (12 mm I.D.) pyrex tube was sealed on one end. The tube was washed with 1 N. HCl, rinsed 4 times with distilled water, necked down about 3 inches from the top and dried for 2 more hours at 120°C.



The hot tube was removed from the oven and clamped in a vertical position. A syringe needle (#15, 12" long) connected to a source of dry nitrogen was inserted to the bottom of the tube. The tube while being purged with dry nitrogen was heated with an air gun for 5 minutes and then the tube was allowed to cool to room temperature. The syringe needle was drawn halfway up the tube and freshly distilled bromodichloroacetaldehyde (4.0 ml, 40 mole) was added with a dry syringe (12" needle). Care was taken to prevent the aldehyde from contaminating the necked down area of the tube. Antimony pentachloride (0.4 ml of a 1 molar solution in dichloromethane, 0.4 mmole, 1 mole percent) was added with a dry syringe as a layer on top of the aldehyde in order to minimize mixing. The syringe needle connected to the nitrogen was withdrawn and the tube was closed off with a short length of butyl rubber tubing and a pinch clamp. The tube was inserted in a liquid nitrogen bath, sealed at 15 mm pressure, removed from the cooling bath inserted into a  $-52^{\circ}$  methyl methacrylate dry ice slush bath and left there for five minutes to allow the temperature in the tube to reach  $-52^{\circ}$ . The tube was then shaken



and replaced in the  $-52^{\circ}$  bath for 10 minutes. The tube was removed and placed in the refrigerator at  $-10^{\circ}\text{C}$  for 1 week to complete the polymerization.

The polymerization tube was opened and cut into 6 sections along the length of the polymer plug. The hard porcelain-like polymer was removed from each section with a spatula and placed in an Erlenmeyer flask (125 ml) in acetone (50 ml). The solid was soaked in acetone for 30 minutes at room temperature. The acetone was heated to boiling and the hot slurry was shaken and then filtered through a M (10-15 u) fritted funnel. The white solid collected was transferred to a 125 ml Erlenmeyer flask containing dichloromethane (30 ml). The filtrate was cooled to room temperature and poured into petroleum ether (30 ml) and the mixture was allowed to stand for 5 minutes.

The acetone insoluble fraction in dichloromethane was collected on a M fritted funnel and was dried in a nitrogen stream. The polymer was then extracted in a stoppered 125 ml Erlenmeyer flask in dichloromethane (45 ml) for 24 hours. The solid was collected on a M fritted funnel, dried in a nitrogen stream, and then kept overnight in a vacuum

desiccator at 15 mm pressure. Polydichlorobromoacetaldehyde was obtained as white granules (1.38 g, 31% yield). An infrared spectrum (KBr) showed absorptions at 3200-3500 (b, v w) (OH stretch), 2944  $\text{cm}^{-1}$  (w); 1350  $\text{cm}^{-1}$  (m), and 1311  $\text{cm}^{-1}$  (s) (C-H band); 1109  $\text{cm}^{-1}$  (vs); 1068  $\text{cm}^{-1}$  (vs); 1052  $\text{cm}^{-1}$  (vs); 949  $\text{cm}^{-1}$  (vs) (C-O stretch); 810  $\text{cm}^{-1}$  (s) (C-C stretch); 789  $\text{cm}^{-1}$  (s), 753  $\text{cm}^{-1}$  (s) (C-Cl stretch); 664  $\text{cm}^{-1}$  (s) (C-Br stretch); 557  $\text{cm}^{-1}$  (m); 440  $\text{cm}^{-1}$  (w); 324  $\text{cm}^{-1}$  (w).

#### Soluble fraction

The acetone soluble fraction precipitated when the filtrate above was poured into petroleum ether. The precipitated solid was collected on a M (10-15 u) fritted funnel dried in a nitrogen stream, and then placed in a small beaker which was kept in a vacuum desiccator for 16 hours at 15 mm pressure. The acetone soluble product was obtained as a white solid (1.20 g, 27%).

The infrared spectrum (KBr) showed absorptions at 3200-3550  $\text{cm}^{-1}$  (b, m) OH stretch; 2944  $\text{cm}^{-1}$  (m) (COH stretch); 1370  $\text{cm}^{-1}$  (w); 1350  $\text{cm}^{-1}$  (m), 1311  $\text{cm}^{-1}$  (s) (C-H bend);

1109  $\text{cm}^{-1}$  (vs), 1068  $\text{cm}^{-1}$  (vs), 1052  $\text{cm}^{-1}$  (vs), 949  $\text{cm}^{-1}$  (vs) (C-O stretch); 810  $\text{cm}^{-1}$  (s) (C-C stretch); 789  $\text{cm}^{-1}$  (s), 753  $\text{cm}^{-1}$  (0) (C-Cl stretch); 664  $\text{cm}^{-1}$  (s) (C-Br stretch); 557  $\text{cm}^{-1}$  (m).

11. Polymerization of  $\text{Cl}_2\text{CBrCHO}$  with  $\text{CF}_3\text{SO}_3\text{H}$  in  $\text{CH}_2\text{Cl}_2$

To a 100 ml round bottom flask with a male 19/32 standard taper joint was washed with dilute (1N) HCl, rinsed with distilled water four times, and dried for 72 hours at 120°C. A 3 way ground glass stopcock with a 19/32 female joint was also washed with dilute (1N) HCl and rinsed four times with distilled water and dried at 120°C for 72 hours. The flask was joined to the stopcock while both were still hot and the assembly was purged with dry nitrogen. The assembly was clamped and allowed to cool to room temperature under a nitrogen blanket. Freshly distilled bromodichloroacetaldehyde (10 ml, 0.1 mole), dry dichloromethane (10 ml) and trifluoromethanesulfonic acid (0.1 ml, mole) was added under nitrogen with dry syringes. The flask was shaken and a small quantity of white powder formed immediately after shaking. The flask was allowed



to stand for 24 hours at  $-30^{\circ}\text{C}$  in a bromobenzene-dry ice slush bath. The flask was removed from the bath and allowed to warm to room temperature. The solid was collected on a fine fritted funnel, washed with acetone (100 ml) and dried under a nitrogen stream. Polybromodichloroacetaldehyde was obtained as a white powder of fine particle size. Yield: 1.54 g, 40%. The infrared spectrum (KBr) showed absorptions at:  $2944\text{ cm}^{-1}$  (m) (C-H stretch);  $1370\text{ cm}^{-1}$  (w);  $1350\text{ cm}^{-1}$  (m) and  $1311\text{ cm}^{-1}$  (s) (C-H bend);  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1052\text{ cm}^{-1}$  (vs),  $949\text{ cm}^{-1}$  (vs) (C-O stretch);  $810\text{ cm}^{-1}$  (s) (C-C stretch);  $789\text{ cm}^{-1}$  (s),  $753\text{ cm}^{-1}$  (s) (C-Cl stretch);  $664\text{ cm}^{-1}$  (s) (C-Br stretch);  $557\text{ cm}^{-1}$  (m),  $440\text{ cm}^{-1}$  (w),  $324\text{ cm}^{-1}$  (w).

12. Polymerization of Bromodichloroacetaldehyde with Pyridine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Procedure #9.

Bromodichloroacetaldehyde (2 ml, 20 mole) was added with a dry syringe (12" needle). Pyridine (0.4 ml of a 1 molar solution in toluene 0.4 mmole or 2 mole percent) was added with a dry syringe as a layer on top of the aldehyde



in order to minimize mixing. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the cooling bath and allowed to come to room temperature. The tube was placed in a 50°C bath for 5 minutes and then removed, shaken quickly, and then placed in a bromobenzene-dry ice slush bath at -30°C for three hours. A self supporting gel formed after 5 minutes and the polymerization was allowed to proceed for 3 hours to complete the reaction.

The sealed tube was warmed to room temperature and was then cut into sections about 1 inch long with a glass file. The sections of tubing containing the polymer were soaked in acetic anhydride (10 ml) - acetone (10 ml) mixture in an Erlenmeyer flask for 24 hours at -10°C. The polymer remained in the glass tubes during this extraction. The glass tube sections were then transferred to a second flask and dichloromethane (20 ml) was added, extracted for 24 hours in CH<sub>2</sub>Cl<sub>2</sub> at 25°C and then dried for 3 hours. The cylindrical sections of polymer were removed from the tubing and then dried in a vacuum desiccator at 15 mm for 16 hours. Polybromodichloroacetaldehyde was obtained as

colorless translucent tough cylinders in the shape of the glass tubing (yield: 2.76 g, 72%). This experiment was repeated and a yield of 68% was obtained. The infrared spectrum (KBr) showed absorption at  $2944\text{ cm}^{-1}$  (m) (C-H stretch),  $1370\text{ cm}^{-1}$  (w),  $1350\text{ cm}^{-1}$  (m) and  $1311\text{ cm}^{-1}$  (s) (C-H bend),  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1052\text{ cm}^{-1}$  (vs),  $949\text{ cm}^{-1}$  (vs) (C-O stretch),  $810\text{ cm}^{-1}$  (s) (C-C stretch),  $789\text{ cm}^{-1}$  (s) (C-Cl stretch),  $753\text{ cm}^{-1}$  (s) (C-Cl stretch),  $664\text{ cm}^{-1}$  (s) (C-Br stretch),  $557\text{ cm}^{-1}$  (m),  $440\text{ cm}^{-1}$  (w),  $324\text{ cm}^{-1}$  (w).

13. Polymerization of Bromodichloroacetaldehyde with Lithium tert-Butoxide.

A 12 inch long (10 mm I.D.) pyrex tube prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (2 ml, 20 mmole) was added with a dry syringe (12" needle). A solution of freshly sublimed lithium tert-butoxide (0.33 ml of a 0.3 solution in methylcyclohexane) (0.1 mmole, 0.5 mole percent) was added carefully as a layer on top of the aldehyde in order to minimize mixing. The tube was inserted in a liquid nitrogen bath and sealed at 0.1 mm pressure,

removed from the cooling bath, warmed slightly and then placed in a bromobenzene-dry ice slush bath (maintained at  $-30^{\circ}\text{C}$ ) for 10 minutes. The tube was then removed, shaken quickly, and placed in the  $-30^{\circ}\text{C}$  bath without agitation for three hours and was not disturbed. A self-supporting gel formed after a few seconds. The gel was clear after a few seconds, and translucent after 3 minutes.

The tube was warmed to room temperature and was cut into sections about 1 inch long with a glass file. The sections of tubing containing the polymer were soaked in an acetic anhydride (10 ml) - acetone (10 ml) mixture in an Erlenmeyer flask with a ground glass stopper for 24 hours at  $-10^{\circ}\text{C}$ , placed in dichloromethane (30 ml) in a stoppered flask at  $25^{\circ}\text{C}$  for 24 hours. The sections were then removed and air dried. The polymer could be tapped out of the glass tubing when dry. Polybromodichloroacetaldehyde (3.04 g, 80% yield) was obtained as colorless translucent cylinders in the shape of the glass tubing. The infrared spectrum (KBr) showed absorptions at  $2944\text{ cm}^{-1}$  (m) (C-H stretch);  $1370\text{ cm}^{-1}$  (w);  $1350\text{ cm}^{-1}$  (m) and  $1311\text{ cm}^{-1}$  (s) (C-H bend);  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),



1052  $\text{cm}^{-1}$  (vs), 949  $\text{cm}^{-1}$  (vs) (C-O stretch); 810  $\text{cm}^{-1}$  (s) (C-C stretch); 789  $\text{cm}^{-1}$  (s), 753  $\text{cm}^{-1}$  (s) (C-Cl stretch); 664  $\text{cm}^{-1}$  (s) (C-Br stretch); 557  $\text{cm}^{-1}$  (m).

14. Polymerization of Bromodichloroacetaldehyde with 2,4,6-collidine.

A 12 inch long (10 mm I.D.) pyrex tube prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe followed by careful addition of 2, 4,6-collidine (0.4 ml of a 1M solution in toluene, 0.4 mmole, 2.0 mole %). The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a  $-30^{\circ}\text{C}$  bath for without agitation 24 hours. A slow gel-forming polymerization took place.

The tube was allowed to warm to room temperature and the tube was cut open with a glass file. The tube was cut into sections along the length of the solid product. The glass sections were soaked in acetone (20 ml) and acetic anhydride for 24 hours at  $-10^{\circ}\text{C}$ . The product was pushed



out of the short sections of pyrex tubing into the acetic anhydride-acetone mixture, isolated on a M fritted funnel, dried, and soaked in dichloromethane (25 ml) for 12 hours at 25°C, collected. After drying in a vacuum desiccator at 15 mm overnight polybromodichloroacetaldehyde was obtained as small white granules (2.61 g, 68% yield).

The infrared spectrum (KBr) could be superimposed on infrared spectra (KBr) of a previously prepared sample of polybromodichloroacetaldehyde.

15. Polymerization of Bromodichloroacetaldehyde with Triethyl amine.

A 12 inch (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (4.0 ml, 40 mmole) was added with a dry syringe and triethyl amine (2 drops) was then added.

The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a -30°C bath for 3 hours. A rapid gel forming polymerization took place.

The tube was allowed to warm to room temperature and the tube was cut open with a glass file. The reaction tube was cut into 1 inch sections along the length of the polymer. The glass sections were soaked in methanol (25 ml) and 36% HCl (5 drops) in a stoppered Erlenmeyer flask for 16 hours at  $-10^{\circ}\text{C}$ . The sections of polymer were extracted in dichloromethane (120 ml) for 24 hours. The polymer was collected and dried. Polybromodichloroacetaldehyde was obtained as cylindrical sections in the shape of the glass tube. (1.99 g, 52%). The infrared spectrum (KBr) could be superimposed on infrared spectra (KBr) of a previously prepared sample of polybromodichloroacetaldehyde. This experiment was repeated and a yield of 57% was obtained.

16. Polymerization of Bromodichloroacetaldehyde with Cesium Chloride.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe. Cesium chloride (0.2 ml of a 0.3 molar solution in tetraglyme, 0.06 mmole or 0.3 mole percent) was then added carefully. The tube

was inserted in a liquid nitrogen bath, sealed at 0.1 pressure, then allowed to come to room temperature. The tube shaken to mix the reactants thoroughly and was then placed in a  $-30^{\circ}\text{C}$  bath for 3 hours. A rapid polymerization took place. The tube was allowed to warm to room temperature and the tube was cut open with a glass file. The tube was cut into sections along the length of the solid product. The glass sections were soaked in acetone (20 ml) and acetic anhydride for 24 hours at  $-10^{\circ}\text{C}$ . The product was pushed out of the short sections of pyrex tubing into the acetic anhydride-acetone mixture. The product was collected on a M fritted funnel and dried in a stream of nitrogen, was soaked in dichloromethane (25 ml) for 12 hours at  $25^{\circ}\text{C}$ , collected and dried. Polybromodichloroacetaldehyde was obtained as small white granules or chips (2.09 g, 54% yield). The infrared spectrum (KBr) could be superimposed on infrared spectra (KBr) of a previously prepared sample.

17. Polymerization of Bromodichloroacetaldehyde with Triphenyl dichlorovinylphosphoniumchloride.

The phosphonium salt was prepared according to the first step in the procedure above for the synthesis of



dichlorobromoacetaldehyde from chloral and triphenyl phosphine. Dichloromethane was removed from the chloral-triphenyl phosphine 1:1 adduct in a stream of dry nitrogen overnight and the flask was closed with 3 stoppers.

A 6 inch test tube was placed in a dry box. Bromo-dichloroacetaldehyde (approximately 2 ml, 20 mmole) and 0.1 g of the phosphonium salt were added to the test tube. The tube was shaken and placed in a  $-30^{\circ}\text{C}$  bath for 3 hours. The tube was removed from the bath and a mixture of acetone (2 ml) and acetic anhydride (2 ml) was added by syringe through the serum cap on top of the solid plug which had formed and the test tube was placed in the refrigerator at  $-10^{\circ}\text{C}$  for 6 hours. The acetone-acetic anhydride mixture was decanted and the product was dried by a slow stream of nitrogen. The polymer was removed, extracted with acetone in a soxhlet extractor for 12 hours, and dried. Poly-dichlorobromoacetaldehyde was obtained as an opaque slightly yellow plug (1.97 g, 51% yield). An infrared spectrum (KBr) could be superimposed on previous spectra. The yield obtained in a similar experiment run previously was 44%.



18. Polymerization of  $\text{Cl}_2\text{CBrCHO}$  with  $\text{CsF}$

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (2 ml, 20 mmole) was added with a dry syringe. Cesium fluoride (0.2 ml of a 0.3 molar solution in tetraglyme, 0.06 mmole or 0.3 mole percent) was then added carefully and the tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the cooling bath and allowed to come to room temperature. The tube was then shaken thoroughly and replaced in the  $-30^\circ\text{C}$  bath for 3 hours. A very rapid gel-forming polymerization took place.

The tube was warmed to room temperature and the tube was cracked with a hammer. The broken glass was removed and a tough cylinder of polymer was recovered. The polymer was soaked in acetone (20 ml) and acetic anhydride (20 ml) for 24 hours and then in dichloromethane (30 ml) for 24 hours. The polymer was isolated and air dried. Polybromodichloroacetaldehyde was obtained as a white translucent cylinder (2.42 g, 63% yield).

The infrared spectrum (KBr) could be superimposed on

infrared spectra (KBr) of a previously prepared sample.

19. Polymerization of Bromodichloroacetaldehyde with Triphenylphosphine. Initiation at 70°C.

A 12 inch long 10 mm I.D. pyrex tube was prepared as described in Experiment #9.

Freshly distilled bromodichloroacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe. A lower half of the tube was heated in an oil bath at 70°C for 5 minutes until the temperature in the tube had equilibrated at 70°C. Triphenylphosphine (0.2 ml of a 1 M solution in toluene, 0.2 mmole, 1 mole percent) was added with a dry syringe on top of the aldehyde as a layer to minimize premature mixing. The tube was then shaken and placed immediately into the 70°C oil bath again for 1 minute. The tube was removed from the oil bath and quickly placed in a -30°C bromobenzene-dry ice slush bath for 24 hours.

A white porcelain like solid had formed during the period. The tube was cut into several sections along the length of the solid plug of polymer. The sections of tubing still containing the product were placed in a 125 ml Erlenmeyer flask and acetic anhydride (30 ml) and acetone

(30 ml) were poured on top. The flask was closed with a stopper and was allowed to stand at  $-10^{\circ}\text{C}$  for 6 hours in the refrigerator. The flask was removed from the refrigerator and the acetone-acetic anhydride and the polymer isolated, extracted with dichloromethane, filtered and dried. Polydichlorobromoacetaldehyde was obtained as white grains (2.06 g, 54% yield). The infrared spectrum could be superimposed on previous spectra for polydichlorobromoacetaldehyde.

20. Attempted Polymerization of Bromodichloroacetaldehyde with Triphenylphosphine Bromodichloroacetaldehyde 1:1 Adduct.

To a dried 500 ml round bottom flask was added a nitrogen blanket triphenylphosphine (27.0 g, 0.1 mole) in dry dichloromethane (60 ml). The flask was cooled at  $0^{\circ}\text{C}$  and the solution was stirred. Bromodichloroacetaldehyde (10 ml, 0.1 mole) was added dropwise over a period of 30 minutes and the solution brought to dryness under a nitrogen stream.

A 6 inch test tube was prepared. Bromodichloroacetaldehyde (2 ml, 20 mmole) was transferred from the vial to



the test tube with the syringe. Approximately 0.1 g of the phosphonium salt was added to the test tube. The flask was closed with the stopper, shaken until the slight cloudiness vanished, and placed in a  $-30^{\circ}\text{C}$  bath for 24 hours. No solid polymer was detected and no polymerization had occurred.

21. Attempted Polymerization of Bromodichloroacetaldehyde with Triphenylphosphine. Initiation at  $25^{\circ}\text{C}$ .

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromodichloroacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe. Triphenylphosphine (0.4 ml of a 0.3 M solution in cyclohexane, 0.12 mmole, 0.6 mole percent) was added with a dry syringe followed by toluene (0.2 ml). The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice-isopropyl alcohol bath for 144 hours. No polymerization had occurred after 144 hours.

The experiment was repeated with a 1 mole percent



concentration of triphenylphosphine, without any indication of polymer formation.

22. Attempted Polymerization of Bromodichloroacetaldehyde with Triphenyldibromovinylphosphoniumbromide.

To a dried 500 ml round bottom flask was dried at 120°C for 72 hours. The flask was removed from the oven and clamped. A nitrogen inlet tube was placed in the left neck, a condenser connected to a bubbler tube was placed in the right neck and an addition funnel placed in the center neck. The flask was purged with nitrogen and heated with an air gun for five minutes. Triphenylphosphine (27.0 g, 0.1 mole) in dry dichloromethane (60 ml) was added from the addition funnel, the flask was cooled to 0°C and the solution was stirred under the nitrogen blanket. Bromal (10 ml, 0.1 mole) was added dropwise over a period of 30 minutes and the solution was brought to dryness.

Bromodichloroacetaldehyde (2 ml, 20 mmole) was transferred from a sealed vial to the test tube in a dry box with the syringe. About 0.1 g of the phosphonium salt was added to the test tube. The tube was shaken until the slight cloudiness vanished, placed in a -30°C bath for 3

hours. The reaction mixture was unchanged at the end of this time. The tube was allowed to remain in the  $-30^{\circ}\text{C}$  bath for 21 additional hours. No solid material was observed.

## E. COPOLYMERIZATION OF BROMODICHLOROACETALDEHYDE

### 23. Copolymerization of Bromodichloroacetaldehyde and Chloral with $\text{AlCl}_3$ .

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled chloral (2 ml, 20 mmole) bromodichloroacetaldehyde (2 ml, 20 mmole), and 0.1 ml of  $\text{AlCl}_3$  in nitrobenzene (1M solution of  $\text{AlCl}_3$ /nitrobenzene, 0.1 mmole, 0.5 mol percent) were added with dry syringes. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry ice-chlorobenzene slush bath at  $-45^\circ\text{C}$  for 24 hours. A gel was formed after one hour.

The tube was warmed to room temperature and was then cut into sections about one inch long. The sections were soaked in acetone (30 ml) for 24 hours at room temperature, and dried for 16 hours at  $25^\circ\text{C}$ . The chloral bromodichloroacetaldehyde copolymer was obtained as translucent tough cylinders in the shape of the polymerization tube (5.07 g, 74.4%). The infrared spectrum showed absorptions at 2940

$\text{cm}^{-1}$  (m) (C-H Stretching);  $1375 \text{ cm}^{-1}$  (w),  $1344 \text{ cm}^{-1}$  (m),  $1305 \text{ cm}^{-1}$  (s) (C-H bending);  $1097 \text{ cm}^{-1}$  (vs),  $1058 \text{ cm}^{-1}$  (vs)  $1040 \text{ cm}^{-1}$  (vs),  $950 \text{ cm}^{-1}$  (vs) (C-O stretching),  $805 \text{ cm}^{-1}$  (s),  $780 \text{ cm}^{-1}$  (s),  $740 \text{ cm}^{-1}$  (s) (C-Halogen stretching),  $650 \text{ cm}^{-1}$  (m).

24. Copolymerization of Dichlorobromoacetaldehyde and Chloral with Trifluoromethanesulfonic acid.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled chloral (1 ml, 10 mmole) bromodichloroacetaldehyde (1 ml, 10 mmole) and 0.1 ml of  $\text{CF}_3\text{SO}_3\text{H}$  (1M solution of  $\text{CF}_3\text{SO}_3\text{H}$  dichloromethane, 0.1 mmole, 1.0 mol percent) were added with dry syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in the refrigerator at  $-10^\circ\text{C}$  for two weeks.

The tube was warmed to room temperature and was then cut into sections about one inch long. The sections were soaked in acetone (30 ml) for 24 hours at room temperature, and dried for 16 hours at  $25^\circ\text{C}$ . The chloral-bromodichloroacetaldehyde copolymer was obtained as white granules



(1.24 g, 36.6% yield). The infrared spectrum showed absorptions at  $2940\text{ cm}^{-1}$  (C-H stretching),  $3460\text{ cm}^{-1}$  (w) (OH stretch end group);  $1375\text{ cm}^{-1}$  (w);  $1344\text{ cm}^{-1}$  (m),  $1305\text{ cm}^{-1}$  (s) (C-H bend);  $1097\text{ cm}^{-1}$  (vs),  $1058\text{ cm}^{-1}$  (vs),  $1040\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $805\text{ cm}^{-1}$  (s),  $780\text{ cm}^{-1}$  (s),  $740\text{ cm}^{-1}$  (s) (C-halogen stretching);  $650\text{ cm}^{-1}$  (m).

25. Copolymerization of Bromodichloroacetaldehyde and Phenyl Isocyanate (10% isocyanate in feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromodichloroacetaldehyde (4.0 ml, 40 mmole) was added with a dry syringe (12" needle). Phenylisocyanate (0.4 ml, 4 mmole, 10%) was added with a dry syringe and the tube was shaken briefly. Pyridine (0.8 ml of a 1M solution in toluene, 0.8 mmole, 2 mole percent) was added as a layer on top of the monomer mixture. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice-acetone bath at  $-78^{\circ}\text{C}$ . A self

supporting gel formed in 30 seconds and no visible change took place after 1 hour. The tube was allowed to remain for 24 hours to complete the reaction. The tube was removed from the cold and was allowed to warm to room temperature. The polymerization tube was cut into one inch sections. The polymer was soaked in acetone (25 ml) for 8 hours. The bromodichloroacetaldehydephenyl isocyanate copolymer was obtained as small white translucent cylinders (4.03 g, 68% yield). A previous experiment, in which the amounts of the reactants were one third of the quantities used here, yielded this copolymer (74%) as small cylinders with a slight red color which could not be extracted.

An infrared spectrum of this copolymer showed absorptions at  $2955\text{ cm}^{-1}$  (m),  $2870\text{ cm}^{-1}$  (w) (C-H Stretching),  $1745\text{ cm}^{-1}$  (s) (carbonyl stretch, urethane),  $1601\text{ cm}^{-1}$  (m),  $1490\text{ cm}^{-1}$  (m) (monosubstituted phenyl),  $1430\text{ cm}^{-1}$  (m),  $1370\text{ cm}^{-1}$  (w),  $1350\text{ cm}^{-1}$  (m),  $1311\text{ cm}^{-1}$  (s) (C-H bending, acetal carbon),  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1052\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $810\text{ cm}^{-1}$  (s),  $789\text{ cm}^{-1}$  (vs),  $752\text{ cm}^{-1}$  (C-Cl stretching),  $664\text{ cm}^{-1}$  (m). Anal. for N: 1.23% which corresponds to about 14% isocyanate in the copolymer.

26. Copolymerization of Dichlorobromacetaldehyde and Chloral with H<sub>2</sub>SO<sub>4</sub>.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled chloral (2 ml, 20 mmole) dichloroacetaldehyde (2 ml, 20 mmole) and two drops of H<sub>2</sub>SO<sub>4</sub> were added with dry syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in the refrigerator for 2 weeks at -10°C.

The tube was warmed to room temperature, was then cut into sections about one inch long. The sections were soaked in acetone (30 ml) for 24 hours at room temperature, and dried for 16 hours at 25°C. Chloral bromodichloroacetaldehyde copolymer was obtained as a white powder, 2.53 g, 37%. The infrared spectrum showed absorptions at 3550-3200 cm<sup>-1</sup> (w, b) (OH stretching, end group), 2940 cm<sup>-1</sup> (m) (C-H stretching); 1375 cm<sup>-1</sup> (w), 1344 cm<sup>-1</sup> (m), 1305 cm<sup>-1</sup> (s) (C-H bending), 1097 cm<sup>-1</sup> (vs), 1058 cm<sup>-1</sup> (vs), 1040 cm<sup>-1</sup> (vs), 950 cm<sup>-1</sup> (vs) (C-O stretching), 805 cm<sup>-1</sup> (s), 780



$\text{cm}^{-1}$  (s),  $740 \text{ cm}^{-1}$  (s) (C-halogen stretching);  $650 \text{ cm}^{-1}$  (m).

27. Copolymerization of Bromodichloroacetaldehyde and Chloral with Pyridine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled chloral (2 ml, 20 mmole) bromodichloroacetaldehyde (2 ml, 20 mmole) and 0.1 ml of pyridine (1M solution of pyridine in toluene 0.1 mmole, 0.5 mol percent) were added with dry syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry ice-chlorobenzene slush bath at  $-45^{\circ}\text{C}$  for 24 hours. A gel was formed after one hour.

The tube was warmed to room temperature and was then cut into sections about one inch long. The sections were soaked in acetone (30 ml) for 24 hours at room temperature, and dried for 16 hours at  $25^{\circ}\text{C}$ . Chloral-bromodichloroacetaldehyde copolymer was obtained as translucent tough cylinders in the shape of the polymerization tube (4.76 g, 70.6%). The infrared spectrum showed absorptions at 2940



$\text{cm}^{-1}$  (m) (C-H stretching);  $1375 \text{ cm}^{-1}$  (w),  $1344 \text{ cm}^{-1}$  (m),  $1305 \text{ cm}^{-1}$  (s) (C-H bending),  $1097 \text{ cm}^{-1}$  (vs),  $1058 \text{ cm}^{-1}$  (vs),  $1040 \text{ cm}^{-1}$  (vs),  $950 \text{ cm}^{-1}$  (vs) (C-H stretching),  $805 \text{ cm}^{-1}$  (s),  $780 \text{ cm}^{-1}$  (s),  $740 \text{ cm}^{-1}$  (s) (C-halogen stretching),  $650 \text{ cm}^{-1}$  (m).

28. Copolymerization of Bromodichloroacetaldehyde and Phenylisocyanate (5% Isocyanate in Feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromodichloroacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe. Phenylisocyanate (0.1 ml, 1 mmole, 5%) was added with a dry syringe (8" needle) and the tube was shaken briefly. Pyridine (0.4 ml of a 1M solution in toluene 0.4 mmole, 2 mole percent) was added as a layer on top of the monomer mixture. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice-acetone bath at  $-78^{\circ}\text{C}$ . A self supporting gel formed in 15 seconds and no visible change took place after one hour. The tube was allowed to remain

in the cold bath for 24 hours and was allowed to warm to room temperature. The polymerization tube was cut into one inch sections. The polymer was soaked in acetone (25 ml) in a stoppered flask for 8 hours, dried in a nitrogen stream broken up, soaked in acetone for 16 hours, collected and dried. Bromodichloroacetaldehyde-phenylisocyanate copolymer was obtained as small translucent grains with a trace of red color which could not be extracted (2.61 g, 65% yield).

An infrared specimen of this copolymer showed absorptions at  $2955\text{ cm}^{-1}$  (m),  $2870\text{ cm}^{-1}$  (m) (C-H stretching),  $1745\text{ cm}^{-1}$  (carbonyl),  $1601\text{ cm}^{-1}$  (w),  $1495\text{ cm}^{-1}$  (w) (aromatic),  $1430\text{ cm}^{-1}$  (w),  $1370\text{ cm}^{-1}$  (w),  $1350\text{ cm}^{-1}$  (m),  $1311\text{ cm}^{-1}$  (s) (C-H bending),  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1052\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $810\text{ cm}^{-1}$  (s),  $789\text{ cm}^{-1}$  (vs),  $752\text{ cm}^{-1}$  (C-Cl stretching),  $664\text{ cm}^{-1}$  (m) (C-Br stretching). Anal. for N: 0.62%. This corresponds to about 9% isocyanate in the copolymer. Analysis for nitrogen at this concentration is no better than  $\pm 0.30$ .

29. Copolymerization of Bromodichloroacetaldehyde and Phenylisocyanate (20% Isocyanate in Feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared.

Freshly distilled bromodichloroacetaldehyde (1 ml, 10 mmole) was added with a dry syringe. Phenyl isocyanate (0.2 ml, 2 mmole, 20%) was added with a dry syringe and the tube was shaken briefly. Pyridine (0.2 ml of a 1M solution in toluene, 0.2 mmole, 2 mole percent) was added by dry syringe as a layer on top of the monomer mixture. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice-acetone bath at  $-78^{\circ}\text{C}$ . A self supporting gel formed after 5 minutes and no visible change took place after 12 hours. The tube was allowed to remain in the cold bath for 24 hours to complete the reaction. The tube was removed from the cold bath and was allowed to warm to room temperature. The polymerization tube was cut into one inch sections along the length of the product. The sections containing the polymer were soaked in acetone (25 ml) in a stoppered flask for 8 hours. The



acetone was decanted into a small beaker and was set aside to evaporate. The one inch sections were dried in a nitrogen stream and then the product was chipped out, with great difficulty, with a microspatula. The small pieces of polymer were soaked in acetone for 16 hours, collected on a C (40-60 u) fritted funnel, and dried in a stream of nitrogen. The remaining acetone was removed from the polymer at 15 mm in a vacuum desiccator overnight. The bromodichloroacetaldehyde-phenylisocyanate copolymer was obtained as small translucent chunks with a slight red color which could not be extracted (1.51 g, 70.6% yield).

The infrared spectrum showed absorptions at  $2950\text{ cm}^{-1}$  (m),  $2870\text{ cm}^{-1}$  (w) (C-H stretching),  $1740\text{ cm}^{-1}$  (s) (C-O stretching, urethane),  $1601\text{ cm}^{-1}$  (m),  $1515\text{ cm}^{-1}$  (w),  $1497\text{ cm}^{-1}$  (m),  $1480\text{ cm}^{-1}$  (w),  $1440\text{ cm}^{-1}$  (w),  $1378\text{ cm}^{-1}$  (w),  $1355\text{ cm}^{-1}$  (m),  $1311\text{ cm}^{-1}$  (s) (C-H bending acetal carbon),  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1052\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $825\text{ cm}^{-1}$  (s),  $797\text{ cm}^{-1}$  (s),  $760\text{ cm}^{-1}$  (s) (C-halogen stretching),  $740\text{ cm}^{-1}$  (m),  $697\text{ cm}^{-1}$  (w),  $668\text{ cm}^{-1}$  (m). Anal. for N: 1.45%.

This corresponds to about 18% isocyanate for the copolymer.



30. Copolymerization of Bromodichloroacetaldehyde and Phenylisocyanate (50% Isocyanate in Feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled phenyl isocyanate (2.1 ml, 2 mmole) was added with a dry syringe (12" needle) and dichlorobromoacetaldehyde (2.0 ml, 2 mmole) was added with dry syringe. The isocyanate was added first and the aldehyde second and good mixing was attained. Pyridine (0.4 ml of a 1 molar solution in toluene, 0.4 mmole or 2 mole percent) was then added carefully as a layer. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry ice-isopropyl alcohol bath at  $-78^{\circ}\text{C}$  for 72 hours. This copolymerization was much slower than the homopolymerization of bromodichloroacetaldehyde and a full 72 hours was required for completion of copolymerization.

The tube was opened and cut into sections with a glass file. The copolymer, a wax, was pushed out of each section into acetone (25 ml) and stirred for 30 minutes. Hexane

(20 ml) was added. The copolymer was then collected on a medium fritted funnel. The copolymer of bromodichloroacetaldehyde and phenyl isocyanate was obtained as a light yellow powder. The infrared spectrum (KBr) showed absorptions at  $2940\text{ cm}^{-1}$  (m) (C-H stretching),  $1730\text{ cm}^{-1}$  (vs) (C=O stretching, urethane),  $1595\text{ cm}^{-1}$  (m),  $1494\text{ cm}^{-1}$  (m) (aromatic, phenyl),  $1370\text{ cm}^{-1}$  (w),  $1342\text{ cm}^{-1}$  (m),  $1305\text{ cm}^{-1}$  (s) (C-H bend, acetal),  $1260\text{-}1270\text{ cm}^{-1}$  (s, b),  $1252\text{ cm}^{-1}$  (s),  $1090\text{-}1100\text{ cm}^{-1}$  (s, b),  $1065\text{ cm}^{-1}$  (vs),  $1047\text{ cm}^{-1}$  (s),  $1005\text{ cm}^{-1}$  (s),  $955\text{ cm}^{-1}$  (vs),  $810\text{ cm}^{-1}$  (s),  $800\text{ cm}^{-1}$  (vs),  $759\text{ cm}^{-1}$  (s),  $700\text{ cm}^{-1}$  (m).

31. Copolymerization of Bromodichloroacetaldehyde with n-butyliisocyanate.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromodichloroacetaldehyde (1.0 ml, 10 mmole), n-butyl isocyanate (1.0 ml, 10 mmole) pyridine (0.2 ml of a 1M solution in toluene 0.2 mmole, 2 mole percent) were added by dry syringe. The tube was closed and was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature.

The tube was shaken to mix the reactants thoroughly and was then placed in a  $-78^{\circ}\text{C}$  bath for 24 hours.

The tube was opened and the hard yellow wax was removed and was stirred for one hour in acetone (20 ml) and the solid material was collected on a fritted funnel. The filtrate was diluted with n-hexane (20 ml) but no solid material precipitated out from the filtrate. The product on the fritted funnel was washed with acetone (25 ml) and dried in a stream of nitrogen. The bromodichloroacetaldehyde-n-butyl-isocyanate copolymer was obtained as light yellow granules (1.18 g, 47.3% yield). The infrared spectrum showed absorptions at  $2940\text{ cm}^{-1}$  (C-H stretching),  $1370\text{ cm}^{-1}$  (w),  $1338\text{ cm}^{-1}$  (m),  $1310\text{ cm}^{-1}$  (s) (C-H bending);  $1105\text{ cm}^{-1}$  (vs),  $1965\text{ cm}^{-1}$  (vs),  $1040\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $820\text{ cm}^{-1}$  (s),  $802\text{ cm}^{-1}$  (s),  $760\text{ cm}^{-1}$  (s) (C-halogen stretching),  $1730\text{ cm}^{-1}$  (m) (C=O stretching, urethane).



F. VACUUM DEGRADATION OF BROMODICHLOROACETALDEHYDE POLYMERS

32. Vacuum Degradation of Polybromodichloroacetaldehyde Obtained from  $\text{Cl}_2\text{CBr CHO}$  and Pyridine.

A 16 inch long pyrex tube (12 mm I.D.) was bent into a U shape. One end of the U-tube was sealed and polybromodichloroacetaldehyde (1.0 g), a powder, was placed in the closed end of the U-tube. The tube was sealed at 0.1 mm pressure. The empty end of the U-tube was placed with one end in a liquid nitrogen bath and the other end, containing the polymer, in a silicone oil bath maintained at  $180^\circ\text{C}$ . After 30 minutes a colorless solid had collected in the cold end of the U-tube; no residue remained in the hot end. The tube was cut open and a sample of the colorless liquid was drawn out with a 10 microliter syringe and immediately injected into a gas chromatograph. The remainder of the colorless liquid was poured into a tared screw cap bottle. The analysis by gas chromatography (35% Diisodecylphthalate on Chromasorb W) indicated that the colorless liquid was 98% monomeric dichlorobromacetaldehyde. An infrared spectrum of the colorless liquid could be nearly



superimposed on previous spectra for the monomer. The polymer had degraded quantitatively (0.97 g or 97%) to monomer without residue formation.

33. Vacuum Degradation of Polybromodichloroacetaldehyde  
Obtained from  $\text{Cl}_2\text{CBrCHO}$  and  $\text{H}_2\text{SO}_4$ .

A 16 inch long pyrex tube (12 mm I.D.) was bent into a U shape. Polybromodichloroacetaldehyde (1.0 g) powder was placed in the closed end of the U-tube and the tube was sealed under at 0.1 mm pressure and the empty end of the tube was placed in a liquid nitrogen bath, and the end containing the polymer was heated with an air gun to approximately  $300^\circ\text{C}$  for 15 minutes, and a char was left behind. The tube was removed from the liquid nitrogen bath and an orange solid was observed. The tube was cut open and a sample of the liquid was drawn out with a 10 microliter syringe and immediately injected into a gas chromatograph. The remainder of the orange liquid was poured into a tared screw cap bottle. The analysis by G.C. indicated that several components were present in the orange liquid including bromodichloroacetaldehyde. The char was removed and weighed (0.17 g). The polymer of bromodichloroacetaldehyde

prepared in the presence of  $\text{H}_2\text{SO}_4$  did not degrade to monomer exclusively. A residue under the more vigorous heating conditions, 17% by weight, remained.

G. POLYMERIZATION RATE DETERMINATION OF  $\text{Cl}_2\text{CBrCHO}$  by NMR

34. Polymerization Rate of Bromodichloroacetaldehyde at  $-30^\circ\text{C}$  by NMR.

A NMR tube was prepared for the experiment according to a consistent cleaning procedure. The NMR tube was soaked in soap solution for 2 days, rinsed repeatedly with distilled water, washed with dilute (1N)  $\text{HNO}_3$ , rinsed again repeatedly with distilled water and finally dried at  $120^\circ\text{C}$  for 72 hours. A 6 inch test tube was cleaned the same way and was dried at  $120^\circ\text{C}$  for 72 hours.

The test tube was removed from the oven and very quickly a serum cap was placed over the open end. The serum cap was firmly anchored to the test tube with copper wire so that the serum cap would not slip off when a syringe needle was inserted through it. A syringe needle (#17, 6 inch) connected to a source of dry nitrogen was inserted through the serum cap and a second syringe needle (#17, 2 inch) was inserted as a nitrogen outlet. The test tube was clamped in a vertical position and the nitrogen flow was started. The tube was purged for 5 minutes and was heated with an air gun. The tube was allowed to cool to room

temperature while a flow of nitrogen was maintained. The tube was then lowered into an oil bath maintained at 50°C. Freshly distilled bromodichloroacetaldehyde (3 ml, 30 mmole) was added with dry syringe through the serum cap and the temperature inside the test tube was allowed to reach 50°C during five minutes. Pyridine (0.6 ml of a 1M solution in toluene, 2 mol percent, 0.6 mmole) was added with a dry syringe and the tube was agitated until the mixing was complete. The NMR tube was removed from the oven, clamped in a vertical position and purged with dry nitrogen for 3 minutes by means of a syringe needle (8 inch, #20). The NMR tube was placed in the 50°C oil bath to a depth of 3 inches. The initiated solution was then transferred from the test tube with a dry syringe to the NMR tube so that 2-1/2 inches of the NMR tube were filled with initiated monomer. The syringe needle connected to the nitrogen source was removed and very quickly the tube was closed with a pressure cap. The top of the NMR tube was wrapped with parafilm. The 50°C bath the NMR tube, and the test tube were carried together to the NMR spectrometer. The NMR tube was removed from the 50°C bath, wiped off and the



zero time aldehyde proton ( $\delta = 8.9$ ) intensity was recorded. The frequency of the methyl group protons on the toluene was used as an internal standard. The NMR tube was placed in a  $-30^{\circ}\text{C}$  bath after 2, 5, 10, 20, 50, 60, 120, and 360 minutes and the aldehyde peak intensity was determined by integration. The toluene methyl peak was also integrated each time. The NMR tube was kept in the  $-30^{\circ}\text{C}$  bath for 72 hours and a final aldehyde peak intensity was determined to obtain a final conversion. The polymerization was actually complete in one hour.

## H. STABILIZATION OF BROMODICHLOROACETALDEHYDE POLYMERS

### 35. Treatment of Bromodichloroacetaldehyde Oligomer with Acetic Anhydride.

Bromodichloroacetaldehyde oligomer (1.8 g, 10 mmole) and acetic anhydride (50 ml) were placed in a 100 ml round bottom flask with a side arm nitrogen inlet. The flask was connected to a source of dry nitrogen and the flask was purged for 10 minutes while a reflux condenser was inserted. The flask was heated with a heating mantle for 15 minutes to have acetic anhydride refluxing gently while all of the solid material went into solution. The flask was allowed to cool to room temperature and acetic anhydride was removed on the rotary evaporator at reduced pressure. The solid remaining in the flask was washed with n-hexane and collected. The polymer was placed in an abderhalden at 0.1 mm pressure at 25°C. End capped (acetone soluble) poly-bromodichloroacetaldehyde was obtained as a white powder (90% yield). The infrared spectrum (KBr) showed absorptions at 2940  $\text{cm}^{-1}$  (m) (C-H stretching), 1753  $\text{cm}^{-1}$  (m) (C=O stretching), 1370  $\text{cm}^{-1}$  (w), 1345  $\text{cm}^{-1}$  (m), 1311  $\text{cm}^{-1}$  (s), 1200  $\text{cm}^{-1}$  (m) (C-O stretching ester end group), 1120  $\text{cm}^{-1}$

(vs),  $1065\text{ cm}^{-1}$  (vs),  $947\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching),  $820\text{ cm}^{-1}$  (s),  $795\text{ cm}^{-1}$  (s),  $765\text{ cm}^{-1}$  (s),  $724\text{ cm}^{-1}$  (m) (C-halogen stretching),  $665\text{ cm}^{-1}$  (w).

36. Treatment of Polybromodichloroacetaldehyde (Prepared from  $\text{H}_2\text{SO}_4$ ) with Acetic Anhydride Without Pyridine.

Bromodichloroacetaldehyde polymer (1.8 g, 10 mmole) and acetic anhydride (50 ml) were placed in a 100 ml round bottom flask with a side arm nitrogen inlet. The flask was connected to a source of dry nitrogen and the flask was purged. A reflux condenser was connected to the neck and the flask was heated with a heating mantle to reflux. The reflux was continued for 15 minutes and then the flask was allowed to cool to room temperature. No polymer came out of the solution while the flask cooled. The polymer was collected, washed with acetone (30 ml) and dried. The polymer was extracted for 24 hours in a soxhlet apparatus with acetone, and dried in an Abderhalden apparatus at  $25^\circ\text{C}$  and 0.1 mm pressure overnight. The end capped polybromodichloroacetaldehyde was obtained as a white powder (1.7 g, 94% yield). An I.R.spectrum showed absorptions at  $2944\text{ cm}^{-1}$  (m) (C-H stretching),  $1753\text{ cm}^{-1}$  (w) (C=O stretching),  $1370$

$\text{cm}^{-1}$  (w),  $1350 \text{ cm}^{-1}$  (m),  $1311 \text{ cm}^{-1}$  (s) (C-H bending),  $1109 \text{ cm}^{-1}$  (vs),  $1068 \text{ cm}^{-1}$  (vs),  $1052 \text{ cm}^{-1}$  (s),  $949 \text{ cm}^{-1}$  (vs), (C-O stretching),  $810 \text{ cm}^{-1}$  (s) (C-C stretching),  $789 \text{ cm}^{-1}$  (s),  $753 \text{ cm}^{-1}$  (s),  $664 \text{ cm}^{-1}$  (s) (C-halogen stretching),  $557 \text{ cm}^{-1}$  (m) (C-Br stretching).



I. THRESHOLD POLYMERIZATION TEMPERATURE DETERMINATION  
FOR  $\text{Cl}_2\text{CBrCHO}$

37. Visual Ceiling Temperature Determination for Bromodichloroacetaldehyde in Toluene with Pyridine.

Four 6 inch test tubes were washed with 1N HCl, rinsed with distilled water four times and dried for 72 hours at  $120^\circ\text{C}$ . The test tube was purged with nitrogen for 10 minutes and then freshly distilled bromodichloroacetaldehyde (3.0 ml, 30 mmole) was added by dry syringe. The lower half of the test tube was then heated in an oil bath at  $50^\circ\text{C}$ . Toluene (2.7 ml) and pyridine (0.3 ml of a 1M solution in toluene 0.3 mmol, 1 mole %) were added by dry syringe. The tube was agitated and placed in an isopropyl alcohol bath at  $50^\circ\text{C}$ . The bath was allowed to cool at  $2^\circ\text{C}$  per minute being stirred rapidly. Small pieces of dry ice were added. At  $-5^\circ\text{C}$  a slight cloudiness was observed in the test tube. Addition of the dry ice was continued until the temperature reached  $-30^\circ\text{C}$ . The test tube was removed from the cold bath and a self supporting gel was observed in the tube. A cloud point at  $-5^\circ\text{C}$  was recorded as the ceiling temperature at a 5 molar monomer concentration.

The second test tube was removed from the oven, closed

with a serum cap, and purged with dry nitrogen by means of a syringe needle connected to nitrogen and an outlet needle. The tube was clamped with the lower half in a 50°C oil bath. Freshly distilled bromodichloroacetaldehyde (3.0 ml, 30 mmole) and pyridine (0.3 ml of a 1M solution in toluene, 0.3 mmole, 1 mole percent) were added with dry syringes while the nitrogen flow was maintained. The tube was agitated and placed in an isopropyl alcohol bath at 50°C. The bath was cooled at 2°C per minute and stirred rapidly. At 23°C a cloudiness was observed. Addition of dry ice was continued until the temperature reached -30°C. The tube was removed from the bath and the tube was broken. An opaque plus of polymer was recovered. The threshold temperature was recorded as  $23^{\circ} \pm 2^{\circ}\text{C}$  for a 9 molar solution of the aldehyde in toluene.

The experiment was repeated using exactly the same procedure. The threshold temperatures for a 6M solution of monomer and a 7.5 M solution of monomer in toluene were determined to be  $4^{\circ} \pm 2^{\circ}\text{C}$  and  $16^{\circ} \pm 2^{\circ}$ , respectively.

38. Instrumental Ceiling Temperature Determination for Bromodichloroacetaldehyde in Toluene with Pyridine

Four 6 inch test tubes were washed in HCl, rinsed with distilled water four times and dried for 72 hours at 120°C.

The test tube was purged with nitrogen for 10 minutes and then freshly distilled bromodichloroacetaldehyde (3.0 ml, 30 mmole) was added by dry syringe. The lower half of the test tube was then heated in an oil bath to 50°C. Toluene (2.7 ml) and pyridine (0.3 ml of a 1M solution in toluene 0.3 mmol, 1 mole 5) were added by dry syringe. The tube was cooled in liquid nitrogen, sealed at 0.1 mm, agitated and placed in an isopropyl alcohol bath at 50°C. The bath was allowed to cool at 2°C per minute while being stirred rapidly. Cold nitrogen as was allowed to pass through a copper coil. The light source was turned on and the intensity of light transmitted through the sample was recorded from the reading on the detector. The flow of cold nitrogen gas was regulated with the temperature probe and controller. The tube was removed from the cold bath and a self supporting gel was observed in the tube. The cloud point at 26°C was recorded as the ceiling temperature



at an 8 molar monomer concentration, where the recorded intensity began to decrease rapidly.

The second tube was removed from the oven, closed with a serum cap, and purged with dry nitrogen. The tube was clamped with the lower half in a 50°C oil bath. Freshly distilled bromodichloroacetaldehyde (3.0 ml, 30 mmole) and pyridine (0.3 ml of a 1M solution in toluene, 0.3 mmole, 1 mole percent) were added with dry syringes. The tube was agitated and placed in an isopropyl alcohol bath at 50°C. The bath was cooled at 2°C per minute and stirred rapidly. The flow of cold nitrogen gas was continued until the temperature reached -30°C. The intensity of light transmitted through the sample was recorded at 1° intervals. The threshold temperature was recorded as 18°C for a 6.7 molar solution of the aldehyde in toluene.

The experiment was repeated using the same procedure. The threshold temperatures for a 5M solution of monomer and a 3M solution of monomer in toluene were determined to be  $11^{\circ} \pm 1^{\circ}\text{C}$  and  $3^{\circ} \pm 1^{\circ}\text{C}$ , respectively.



J. SOLUBILITY FOR  $\text{Cl}_2\text{CBrCHO}$ 39. Solubility Tests for Polybromodichloroacetaldehyde  
(Prepared under Anionic Conditions)

In each of 10 dry Erlenmeyer flasks with ground glass joints were placed 1 gram samples of polybromodichloroacetaldehyde and 10 ml of the solvent to be tested. The solvents acetone, dichloromethane, nitrobenzene, dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol, o-chlorophenol, chloroform, and toluene were added successively to each flask by syringe and the tubes were closed with ground glass stoppers. The flasks were allowed to stand for 72 hours at  $25^\circ\text{C}$ . The solid materials remaining after 72 hours were collected and the PMR spectrum of each filtrate was taken to detect the presence of soluble polymer. The PMR spectra showed solvent peaks, and in some cases small peaks corresponding to the protons in bromodichloroacetaldehyde and the hydrate of this aldehyde. These were the only peaks observed. The acetone, toluene, chloroform and dichloromethane filtrates were evaporated, and in every case a trace of solid remained which was the hydrate of bromodichloroacetaldehyde. The dimethyl

sulfoxide, trifluoroacetic acid, hexafluoroisopropanol and nitrobenzene filtrates were concentrated and the removed completely at reduced pressure. No residues remained behind after complete solvent removal.

The solubility tests were repeated employing mixed solvent systems: acetone/dichloromethane/toluene; dimethyl sulfoxide/benzene; nitrobenzene- and dichlorobenzene. Polychloral samples were also tested for solubilities in these solvent combinations for comparison. No solid material, neither polychloral nor polybromodichloroacetaldehyde could be isolated from the filtrates after the polymers had been exposed for 72 hours to these solvent mixtures.

#### 40. Swelling Tests for Polybromodichloroacetaldehyde Polychloral.

A sample of polychloral, a chloral-phenyl isocyanated copolymer (containing 10% isocyanate according to elemental analysis for nitrogen), polybromodichloroacetaldehyde, and a bromodichloroacetaldehyde-phenyl isocyanate copolymer (containing 10% isocyanate) were covered with dichloromethane in Erlenmeyer flasks. The diameter of each cylinder of polymer was recorded at intervals while the

dichloromethane swelled the samples. After 48 hours no more swelling was observed. The initial and final diameter were recorded. The samples were allowed to dry for one week and the diameter of the redried samples were also recorded. The data were: polychloral; initial diameter 0.495 inches, final 0.525 inches, redried 0.495, 6.1% swelling; chloral-phenylisocyanate copolymer, initial diameter 0.480", final diameter 0.535", redried diameter 0.480", 11.2% swelling; polybromodichloroacetaldehyde initial diameter 0.483", final diameter 0.515", redried diameter 0.483". 6.3% swelling; bromodichloroacetaldehyde phenylisocyanate copolymer initial diameter 0.456", final diameter 0.513" redried diameter 0.456", 12.5% increase.



L. CHLORODIBROMOACETALDEHYDE SYNTHESIS AND  
POLYMERIZATION

41. Synthesis of Chlorodibromoacetaldehyde from  
Chloroacetaldehyde-diethylacetal.

A 500 ml 3-neck round bottom flask was equipped with a pressure-equalizing addition funnel, a nitrogen inlet tube, and a reflux condenser. The flask was purged with dry nitrogen for 10 minutes and then chloroacetaldehyde diethylacetal (100 ml. 0.67 mole) was added and the whole assembly was lowered into an oil bath. The flask was heated with stirring until the oil bath had reached 100°C. Bromine (85 ml. 1.5 mole) was added dropwise at a rate that just allowed the red color in the flask to vanish. The addition was complete after 8 hours.

The flask was removed from the oil bath and was allowed to cool to room temperature. The addition funnel was replaced with a ground glass stopper, the reflux condenser was removed and replaced with an adapter for distillation. The condenser was joined to the adapter on one end and to a 100 ml round bottom receiving flask with a vacuum adapter, which was cooled in a dry ice/Isopropyl alcohol bath. Volatile products were collected at a



pressure of 15 mm in the receiver; the distillation was completed by heating the flask with an oil bath at 40°C. The fraction collected a mixture of ethyl bromide (95%) and ethanol (5).

The receiving flask was replaced with a 200 ml round bottom flask, phosphorous pentoxide (5.0 g) was added and the entire apparatus was purged with dry nitrogen for 5 minutes. The flow of nitrogen was decreased and the flask was cooled in a dry ice/isopropyl alcohol bath. Ethanol was collected while the vapor temperature was less than 100°C, the vapor temperature then rose rapidly. The receiver was replaced with a dry 200 ml. flask and the pressure in the apparatus was reduced to 100 mm; the second fraction was impure chlorodibromoacetaldehyde.

The receiver was now removed from the cold bath and was allowed to warm to room temperature under a blanket of nitrogen. The aldehyde was then distilled from the P<sub>2</sub>O<sub>5</sub> at 100°C 30 mm under nitrogen. The first 3 ml. were collected and the receiver was replaced which was cooled in a dry ice/isopropyl alcohol bath of -78°C. About 30 ml. of colorless liquid was collected as a middle cut. The

aldehyde was redistilled from phosphorous pentoxide (3.0 g) // under nitrogen at 30 mm pressure through a 6 inch vegreaux column. The first 4 ml of chlorodibromoacetaldehyde were discarded and then about 25 ml. of pure aldehyde was collected, a colorless liquid (25.2 ml., 38% yield), boiling at 147-148°C, 760 mm. The infrared spectrum (neat) showed absorptions at 1747  $\text{cm}^{-1}$  (vs) (C=O stretch), 3480  $\text{cm}^{-1}$  (w) (overtone); 2850  $\text{cm}^{-1}$  (m), 650  $\text{cm}^{-1}$  (s). The carbonyl stretch in hexane was 1750  $\text{cm}^{-1}$  and in the gas phase 1768  $\text{cm}^{-1}$ .

The PMR spectrum showed one peak at  $\delta = 8.7$  ppm.

Anal: Calcd. for  $\text{C}_2\text{HBr}_2\text{Cl}_{10}$ : C, 10.17%; H, 0.42; Cl, 15.01%; Br, 67.55%. Found, C, 10.24; H, 0.60; Cl, 14.59; Br, 67.39%.

#### 42. Polymerization of Chlorodibromoacetaldehyde with Pyridine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2 ml, 2 mmole) was added with a dry syringe. Pyridine (0.4 ml. of a 1 molar solution in toluene, 0.4 mmole or 2 mole percent)

was then added, the tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry ice-chlorobenzene slush bath at  $-45^{\circ}\text{C}$  for 72 hours. Self supporting gel formed after 10 minutes; the polymerization was essentially complete after one hour but for completion the polymerization was allowed to proceed for 72 hours.

The tube was warmed to room temperature and was then cut into sections about 1 inch long with a glass file. The sections of tubing containing the polymer was soaked in an acetic anhydride (10 ml.) acetone (10 ml) mixture for 24 hours at  $-10^{\circ}\text{C}$ . The polymer was isolated, washed with acetone (50 ml.), soaked for 24 hours in dichloromethane (20 ml) at  $-10^{\circ}\text{C}$ , filtered and dried. Polychlorodibromoacetaldehyde (2.87 g, 52% yield) was obtained as colorless translucent chips. The infrared spectrum (KBr) showed absorptions at  $2940\text{ cm}^{-1}$  (C-H stretching),  $1338\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$  (C-H bending),  $1105\text{ cm}^{-1}$ ,  $1065\text{ cm}^{-1}$ ,  $1040\text{ cm}^{-1}$ ,  $950\text{ cm}^{-1}$  (vs), (C-O stretching)  $802\text{ cm}^{-1}$  (C-C stretching or C-Cl stretching)  $780\text{ cm}^{-1}$  and  $726\text{ cm}^{-1}$  (C-halogen

stretching). Anal. Calcd. for  $C_2HBr_2Cl_{10}$ : C, 10.17%; H, 0.42%; Cl, 15.01%; Br, 67.66%. Found: C, 10.38%, H, 0.69%; Cl, 15.00%; Br, 67.28%.



M. COPOLYMERIZATION OF CHLORODIBROMOACETALDEHYDE

43. Copolymerization of Chlorodibromoacetaldehyde and Phenyl Isocyanate (10% isocyanate in feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml., 20 mmole) and phenyl isocyanate (0.2 ml., 2 mmole, 10%) were added with a dry syringe and the tube was shaken briefly. Pyridine (0.4 ml. of a 1M solution in toluene, 0.4 mmole, 2 mole percent) was added carefully. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry-ice acetone bath at  $-78^{\circ}\text{C}$ , and allowed to remain undisturbed 72 hours. After warming to room temperature, the polymerization tube was cut into 1 inch sections and soaked in acetone (25 ml) 8 hours, dried, soaked again and dried. Chlorodibromoacetaldehyde phenyl isocyanate copolymer was obtained as small white granules (2.51 g, 54% yield). An infrared spectrum (KBr) showed absorption at:  $2950\text{ cm}^{-1}$  (m),  $2885\text{ cm}^{-1}$  (w) (C-H stretching)  $1745\text{ cm}^{-1}$  (vs) (C=O stretching, urethane);  $1601\text{ cm}^{-1}$  (m),

1550  $\text{cm}^{-1}$  (w), 1528  $\text{cm}^{-1}$  (w), 1497  $\text{cm}^{-1}$  (m), 1430  $\text{cm}^{-1}$  (w) (aromatic); 1373  $\text{cm}^{-1}$  (w); 1355  $\text{cm}^{-1}$  (m), 1318  $\text{cm}^{-1}$  (s) (C-H bending, acetal carbon); 1109  $\text{cm}^{-1}$  (vs), 1068  $\text{cm}^{-1}$  (vs), 1050  $\text{cm}^{-1}$  (vs), 950  $\text{cm}^{-1}$  (vs) (C-O stretching) 810  $\text{cm}^{-1}$  (s); 789  $\text{cm}^{-1}$  (s), 752  $\text{cm}^{-1}$  (s), 747  $\text{cm}^{-1}$  (s), 705  $\text{cm}^{-1}$  (w). Anal. for N: 0.79% (12% of isocyanate in the copolymer).

44. Copolymerization of Chlorodibromoacetaldehyde and Chloral with Trifluoromethanesulfonic Acid.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chloral (2 ml., 20 mmole) Chlorodibromoacetaldehyde (2 ml., 20 mmole), and 0.4 ml. of  $\text{CF}_3\text{SO}_3\text{H}$  (1M solution of  $\text{CF}_3\text{SO}_3\text{H}$  in dichloromethane, 0.4 mmole, 2.0 mole percent) were added with dry syringe. The tube was inserted in a liquid nitrogen bath sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in the refrigerator at  $-10^\circ\text{C}$  for 2 weeks. The tube was warmed to room temperature and was then cut into sections about one inch long, soaked in acetone (30 ml.) and dried. Chloral-chlorodibromoacetaldehyde copolymer was

obtained as a white powder (3.07 g, 41% yield). The infrared spectrum showed absorptions at  $2940\text{ cm}^{-1}$  (m) (C-H stretching);  $1370\text{ cm}^{-1}$  (w),  $1344\text{ cm}^{-1}$  (m),  $1320\text{ cm}^{-1}$  (s) (C-H bending);  $1105\text{ cm}^{-1}$  (vs),  $1070\text{-}1050\text{ cm}^{-1}$  (vs, b),  $947\text{ cm}^{-1}$  (vs, b) (C-O stretching);  $828\text{-}805\text{ cm}^{-1}$  (s, b),  $800\text{ cm}^{-1}$  (s) (C-Cl stretching);  $787\text{ cm}^{-1}$  (m);  $750\text{ cm}^{-1}$  (s, b),  $672\text{ cm}^{-1}$  (m) (C-Br stretching).

45. Copolymerization of Chlorodibromoacetaldehyde and Chloral with  $\text{AlCl}_3$ .

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chloral (2 ml., 20 mmole) chlorodibromoacetaldehyde (2 ml. 20 mmole) and 0.1 ml of  $\text{AlCl}_3$  in nitrobenzene (1M solution of  $\text{AlCl}_3$  nitrobenzene, 0.1 mmole, 0.5 mol percent) were added with dry syringes. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry ice-/chlorbenzene slush bath at  $-45^\circ\text{C}$  for 24 hours. A gel was formed after one hour. The tube was warmed to room temperature and was then cut into sections



about one inch long, soaked in acetone (30 ml) for 24 hours and dried. Chloral-chlorodibromoacetaldehyde copolymer was obtained as translucent, tough cylinders in the shape of the polymerization tube (4.93 g, 66% yield). The infrared spectrum showed absorptions at  $2940\text{ cm}^{-1}$  (m) (C-H stretching)  $1370\text{ cm}^{-1}$  (w);  $1344\text{ cm}^{-1}$  (m),  $1320\text{ cm}^{-1}$  (s) (C-H bending);  $1105\text{ cm}^{-1}$  (vs, b),  $947\text{ cm}^{-1}$  (vs, b) (C-O stretching);  $828\text{--}805\text{ cm}^{-1}$  (s, b),  $800\text{ cm}^{-1}$  (s), (C-Cl stretching);  $787\text{ cm}^{-1}$  (m);  $750\text{ cm}^{-1}$  (s, b),  $672\text{ cm}^{-1}$  (m) (C-Br stretching).

46. Copolymerization of Chlorodibromoacetaldehyde with Phenylisocyanate (5% isocyanate in feed).

a 12 inch long (10 mm I.D.) pyrex tube was prepared according to the procedure in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml, 20 mmole) and phenyl isocyanate (0.1 ml., 0.1 mmole, 5%) and pyridine (2 drops from a #18 needle) were added with syringes. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a chlorobenzene-dry ice bath at  $-45^{\circ}\text{C}$ . for 72 hours. The tube was allowed to warm



to room temperature, cut into one inch sections, soaked in acetone (25 ml.) for 8 hours and dried. Chlorodibromoacetaldehyde-phenyl isocyanate copolymer was obtained as small white granules with a very slight red color that could not be extracted (3.36 g, 75% yield).

An infrared spectrum (KBr) showed absorptions at  $2960\text{ cm}^{-1}$  (m),  $2885\text{ cm}^{-1}$  (w) (C-H stretching);  $1745\text{ cm}^{-1}$  (m), (C-O stretching, urethane);  $1601\text{ cm}^{-1}$  (w),  $1497\text{ cm}^{-1}$  (w) (aromatic);  $1373\text{ cm}^{-1}$  (w);  $1355\text{ cm}^{-1}$  (m),  $1318\text{ cm}^{-1}$  (s) (C-H bending, acetal C-H),  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),  $1050\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-O stretching);  $810\text{ cm}^{-1}$  (s),  $789\text{ cm}^{-1}$  (s),  $752\text{ cm}^{-1}$  (s),  $747\text{ cm}^{-1}$  (s),  $705\text{ cm}^{-1}$  (w). Anal. for N: 0.58%. Corresponding to 9% isocyanate in the copolymer.

47. Copolymerization of Chlorodibromoacetaldehyde with Phenylisocyanate (20% isocyanate in feed).

A 12 inch long (10 mm I.D) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml. 20 mmole) phenylisocyanate (0.4 ml. 4 mmole, 20%) and pyridine (0.4 ml of a 1M solution in toluene, 0.4 mmole 2,

mole percent) were added with syringes, chlorodibromoacetaldehyde (2.0 ml, 20 mmole) and phenyl isocyanate (0.4 ml., 0.4 mmole 20%) and pyridine (2 drops from a #18 needle) was added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a chlorobenzene-dry ice bath at  $-45^{\circ}\text{C}$  for 72 hours. The tube was allowed to warm to room temperature, cut into one inch sections soaked in acetone (25 ml) for 8 hours and dried. Chlorodibromoacetaldehyde-phenyl isocyanate copolymer was obtained as small white granules with a very slight red color that could not be extracted (2.23 g 46.4%). Anal for N: 2.11. Corresponds to 27.3% isocyanate in copolymer. An infrared spectrum (KBr) showed absorption at:  $2950\text{ cm}^{-1}$  (m),  $2885\text{ cm}^{-1}$  (w) (C-H stretching)  $1745\text{ cm}^{-1}$  (vs) (C-O stretching, urethane);  $1601\text{ cm}^{-1}$  (m),  $1550\text{ cm}^{-1}$  (w),  $1528\text{ cm}^{-1}$  (m),  $1497\text{ cm}^{-1}$  (m) (aromatic);  $1430\text{ cm}^{-1}$  (w);  $1373\text{ cm}^{-1}$  (w),  $1355\text{ cm}^{-1}$  (m),  $1318\text{ cm}^{-1}$  (s) (C-H bending, acetal carbon);  $1109\text{ cm}^{-1}$  (vs),  $1068\text{ cm}^{-1}$  (vs),

1052  $\text{cm}^{-1}$  (vs), 950  $\text{cm}^{-1}$  (vs) (C-H stretching); 810  $\text{cm}^{-1}$  (s), 789  $\text{cm}^{-1}$  (vs), 752  $\text{cm}^{-1}$  (vs) (C-Cl stretching); 664  $\text{cm}^{-1}$  (m) (C-Br stretching); 748  $\text{cm}^{-1}$  (s).

48. Copolymerization of Chlorodibromoacetaldehyde and Phenylisocyanate (50% Isocyanate in feed).

Phenylisocyanate (1.1 ml, 1 mmole) and chlorodibromoacetaldehyde (1.0 ml, 1 mmol) were added with dry syringes. The isocyanate was added first, the aldehyde second and good mixing was obtained. Pyridine (0.4 ml of a 1 molar solution in toluene (0.4 mmole or 2 mole percent) was then added carefully. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, allowed to come to room temperature, shaken thoroughly and then placed in a dry ice/isopropyl alcohol bath at  $-78^{\circ}\text{C}$  for 72 hours. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature, shaken to mix the reactants, and then placed in a dry ice/acetone bath at  $-78^{\circ}\text{C}$  for 72 hours. Copolymerization was much slower than the homopolymerization of bromodichloroacetaldehyde and a full 72 hours was required. The tube was opened, cut into sections and the copolymer was stirred



with acetone (25 ml) wax for 30 minutes. During this time the wax became a light orange powdery precipitate. Hexane (20 ml) was added while the stirring was continued. The copolymer was then collected and dried.

The copolymer of chlorodibromoacetaldehyde and phenylisocyanate was obtained as a light yellow powder (3.03 g, 91% yield). The infrared spectrum showed absorptions at:  $2940\text{ cm}^{-1}$  (m) (C-H stretching),  $2870\text{ cm}^{-1}$  (w) (C-H stretching, phenyl);  $1735\text{ cm}^{-1}$  (vs) (C=O stretching, urethane),  $1595\text{ cm}^{-1}$  (m),  $1550\text{ cm}^{-1}$  (w),  $1520\text{--}1525\text{ cm}^{-1}$  (w),  $1495\text{ cm}^{-1}$  (m),  $1442\text{ cm}^{-1}$  (w) (monosubstituted phenyl ring);  $1397\text{ cm}^{-1}$  (w),  $1367\text{ cm}^{-1}$  (w),  $1315\text{ cm}^{-1}$  (m),  $1298\text{ cm}^{-1}$  (s),  $1210\text{ cm}^{-1}$  (w, b),  $1120\text{ cm}^{-1}$  (s),  $1090\text{ cm}^{-1}$  (s),  $1061\text{ cm}^{-1}$  (s),  $965\text{ cm}^{-1}$  (vs),  $820\text{ cm}^{-1}$  (m),  $800\text{ cm}^{-1}$  (m, b),  $768\text{ cm}^{-1}$  (s),  $755\text{ cm}^{-1}$  (vs),  $708\text{ cm}^{-1}$  (s). Anal. for N: 2.96%. This corresponds to 38% isocyanate in the copolymer.

49. Copolymerization of Chlorodibromoacetaldehyde with n-butyliisocyanate.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml,



20 mmole) and n-butyliisocyanate (2.3 ml, 25 mmole) were mixed. Pyridine (0.8 ml of a 1M solution in toluene, 0.8 mmole, 4 mole %) was finally added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, allowed to come to room temperature, briefly shaken and then placed in a  $-78^{\circ}\text{C}$  bath for 24 hours. The tube was allowed to warm to room temperature, cut open and a light yellow soft solid was isolated and placed in a small flask with acetone (10 ml), stirred for one hour. The solid material was collected. The filtrate was poured into hexane (20 ml) but gave no additional solid material. Chlorodibromoacetaldehyde/n-butyliisocyanate copolymer was obtained as a light yellow powder (1.47 g, 22% yield). The infrared spectrum shows absorptions at  $2940\text{ cm}^{-1}$  (C-H stretching);  $1720\text{ cm}^{-1}$  (C=O stretching, urethane);  $1370\text{ cm}^{-1}$  (w);  $1338\text{ cm}^{-1}$  (m),  $1310\text{ cm}^{-1}$  (s) (C-H bending),  $1105\text{ cm}^{-1}$  (vs)  $1065\text{ cm}^{-1}$  (vs),  $1040\text{ cm}^{-1}$  (vs),  $950\text{ cm}^{-1}$  (vs) (C-H stretching);  $802\text{ cm}^{-1}$  (s),  $780\text{ cm}^{-1}$  (s),  $726\text{ cm}^{-1}$  (s) (C-Halogen stretching). Anal. for N: 0.68% (10% isocyanate in copolymer).

50. Attempted Polymerization of Chlorodibromoacetaldehyde with Triphenyl Phosphine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml, 20 mmole) was added with a dry syringe. Triphenyl phosphine (0.4 ml of a 0.3 M solution in cyclohexane, 0.12 mmole, 0.6 mole percent) and toluene (0.2 ml) was added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, allowed to come to room temperature, shaken to mix the reactants thoroughly and then placed in a dry ice/isopropyl alcohol bath for 72 hours. No solid material was noticeable even after additional 72 hours and even after additional 72 hours in spite of very careful work up.

The experiment was repeated with a 1 mole percent concentration of triphenyl phosphine, at  $-78^{\circ}\text{C}$  and at a bath temperature of  $-45^{\circ}\text{C}$  but no polymer was isolated.

N. CHARACTERIZATION OF Br<sub>2</sub>CCl CHO POLYMERIZATIONS

51. Visual Ceiling Temperature Determination for Chlorodibromoacetaldehyde in Toluene with Pyridine.

Four 6 inch test tubes were washed in 1N HCl, rinsed with distilled water four times and dried for 72 hours at 120°C. One tube was removed from the oven and quickly closed with a serum cap. A syringe needle (#17, 8" long) connected to a source of dry nitrogen was inserted as a nitrogen outlet. The test tube was purged with nitrogen for 10 minutes and then freshly distilled chlorodibromoacetaldehyde (2.0 ml, 20 mmole) was added by a dry syringe while the flow of dry nitrogen was maintained. The lower half of the test tube was then heated in an oil bath at 50°C. Toluene (1.7 ml) and pyridine (0.4 ml of a 1M solution in toluene 0.2 mmole, 1 mole %) were added with a dry syringe, the tube was agitated and placed in an isopropyl alcohol bath at 50°C. The bath was allowed to cool at 2°C per minute while being stirred. Small pieces of dry ice were added to the bath while it was stirred rapidly. At -37°C a slight cloudiness was observed in the test tube. Addition of the dry ice was continued until the temperature

reached  $-60^{\circ}\text{C}$ . The test tube was removed from the cold bath and a self supporting gel was observed. A cloud point of  $-37^{\circ}\text{C}$  was recorded as the polymerization temperature at 5 molar monomer concentration.

The second test tube was removed from the oven, closed with a serum cap, and purged with dry nitrogen by means of syringe needle connected to nitrogen and an outlet needle. The tube was clamped with the lower half in a  $25^{\circ}\text{C}$  oil bath. Freshly distilled chlorodibromoacetaldehyde (3.0 ml, 30 mmole) and pyridine (0.3 ml of a 1M solution in toluene, 0.3 mmole, 1 mole percent) were added with dry syringes while the nitrogen flow was maintained. The tube was agitated and placed in an isopropyl alcohol bath at  $25^{\circ}\text{C}$ . The bath was cooled at  $2^{\circ}\text{C}$  per minute and stirred rapidly. At  $-17^{\circ}\text{C}$  a cloudiness was observed. Addition of dry ice was continued until the temperature reached  $-60^{\circ}\text{C}$ . The tube was removed from the bath and the tube was broken. An opaque plug of polymer was recovered. The threshold temperature was recorded as  $-17^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for a 9 mole solution of the aldehyde in toluene.

The experiment was repeated using exactly the same



procedure. The threshold temperatures for a 6M solution of monomer and a 7.5 M solution of monomer in toluene were determined to be  $-35^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and  $-26^{\circ}\text{C} \pm 5^{\circ}\text{C}$  respectively by this procedure.

52. Instrumental Ceiling Temperature Determination for Chlorodibromoacetaldehyde in Toluene with Pyridine. ✓

Four polymerization tubes were washed in 1N HCl, rinsed with distilled water four times and dried for 72 hours at  $120^{\circ}\text{C}$ . One tube was removed from the oven. A syringe needle (#17, 8" long) connected to a source of dry nitrogen was inserted. The test tube was purged with nitrogen for 10 minutes and then freshly distilled chlorodibromoacetaldehyde (3.0 ml, 30 mmole) was added by a dry syringe while the flow of dry nitrogen was maintained. The lower half of the tube was then cooled in liquid nitrogen. Toluene (0.3 ml) and pyridine (0.3 ml of a 1M solution in toluene 0.3 mmole, 1 mole %) were added with a dry syringe, the tube was sealed and placed in an isopropyl alcohol bath at  $50^{\circ}\text{C}$ . The bath was cooled at  $1/2^{\circ}\text{C}$  per minute by a copper coil with a regulated flow cold nitrogen. The intensity of light transmitted through the sample was

recorded. The flow of cold gas continued until the temperature reached  $-60^{\circ}\text{C}$ . The tube was removed from the cold bath and a self supporting gel was observed. A cloud point of  $-12^{\circ}\text{C}$  was recorded as the temperature at a 8.3 molar monomer concentration. At  $-12^{\circ}\text{C}$  the intensity of transmitted light just began to decrease.

The second tube was removed from the oven and purged with dry nitrogen by means of a syringe needle connected to nitrogen. Freshly distilled chlorodibromoacetaldehyde (3.0 ml, 30 mmole) was added and the tube was cooled in liquid nitrogen, pyridine (1.3 ml of a 0.23M solution in toluene, 0.3 mmole, 1 mole percent) was added with a dry syringe while the nitrogen flow was maintained. The tube was warmed to  $25^{\circ}\text{C}$ , agitated and placed in an isopropyl alcohol bath at  $25^{\circ}\text{C}$ . The bath was cooled at  $2^{\circ}\text{C}$  per minute and stirred rapidly, around  $-20^{\circ}\text{C}$  rapid decrease in transmitted light was recorded. Cooling with cold nitrogen gas was continued until the temperature reached  $-60^{\circ}\text{C}$ . The tube was removed from the bath and the tube was broken. An opaque plug of polymer was recovered. The threshold temperature was recorded as  $-20^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for a 6.7 molar solution of the

aldehyde in toluene.

The experiment was repeated using exactly the same procedure. The threshold temperatures for a 5M solution of monomer and a 2.5 M solution of monomer in toluene were determined to be  $-24^{\circ}\pm 2^{\circ}\text{C}$  and  $-30^{\circ}\pm 3^{\circ}\text{C}$  respectively.

53. Polymerization Rate of Chlorodibromoacetaldehyde at  $-78^{\circ}\text{C}$  by NMR.

A NMR tube was prepared for the experiment according to a consistent cleaning procedure. The NMR tube was soaked in soap solution for 2 days, rinsed repeatedly with distilled water, washed with dilute (1 N)  $\text{HNO}_3$ , rinsed again repeatedly with distilled water and finally dried at  $120^{\circ}\text{C}$  for 72 hours. A 6 inch test tube was cleaned the same way and was dried at  $120^{\circ}\text{C}$  for 72 hours.

The test tube was removed from the oven and very quickly, a serum cap was placed over the open end and secured. A syringe needle (#17, 6 inch) connected to a source of dry nitrogen was inserted through the serum cap and a second syringe needle (#17, 2 inch) was inserted as a nitrogen outlet. The test tube was clamped in a vertical position and the nitrogen flow was started. The tube was



purged for 5 minutes, heated with an air gun, allowed to cool to room temperature while a flow of nitrogen was maintained, and lowered into an oil bath maintained at 25°C. Freshly distilled chlorodibromoacetaldehyde (3 ml, 30 mmole) was added with a dry syringe and the temperature inside the test tube was allowed to reach 50°C (five minutes). Pyridine (0.6 ml of a 1M solution in toluene, 2 mol percent, 0.6 mmole) was added and the tube was agitated. The NMR tube was removed from the oven, clamped in a vertical position and purged with dry nitrogen for 3 minutes, was placed in the 50°C oil bath to a depth of 3 inches. The initiated solution was then transferred from the test tube to the NMR tube so that 2-1/2 inches of the NMR tube were filled with initiated monomer. The syringe needle connected to the nitrogen was removed and very quickly the tube was closed with a pressure cap. The top of the NMR tube was wrapped with parafilm. The NMR tube was removed from the 50°C bath, wiped off and the zero time aldehyde proton ( $\delta = 8.9$ ) intensity was recorded. (The methyl group resonances of the toluene was used as an internal standard.) It was then placed in a -78°C bath along with the test tube which



contained the remaining initiated monomer which was used as a blank. The NMR tube was removed from the  $-78^{\circ}\text{C}$  bath after 2, 5, 10, 20, 40, 60, 120, and 360 minutes and the aldehyde peak intensity was determined by integration.

## O. CHARACTERIZATION OF CDBA POLYMERS AND COPOLYMERS

### 54. Vacuum Degradation of Polybromodichloroacetaldehyde Obtained from $\text{Br}_2\text{CClCHO}$ and Pyridine.

A 16 inch long pyrex tube (12 mm I.D.) was bent into a U shape; one end was sealed. Polychlorodibromoacetaldehyde (1.0 g), a powder, was placed in the closed end of the U-tube, and the tube was sealed at 0.1 mm pressure. The empty end of the U-tube was placed in a liquid nitrogen bath and the other end, containing the polymer in a silicone oil bath of  $180^\circ\text{C}$ . After 30 minutes a colorless solid had collected in the cold end of the U-tube. No residue in the hot end of the oil bath. The tube was removed from the baths, warmed to room temperature, the colorless solid was melted and the tube was cut open. A sample of the colorless liquid was drawn out with a 10 microliter syringe and immediately injected into a gas chromatograph. The remainder of the colorless liquid was poured into a tared screw cap bottle (0.97 g or 97%). The analysis by gas chromatography (35% diisodecyl phthalate on Chromosorb W) indicated that the colorless liquid was 98% chlorodibromoacetaldehyde. An infrared spectrum was nearly superimposable on spectra for the pure monomer.

55. Solubility Tests for Chlorodibromoacetaldehyde Homopolymers.

In each of 10 dry Erlenmeyer flasks with ground glass joints samples of poly chlorodibromoacetaldehyde and 10 ml of the solvent to be tested. The solvents acetone, dichloromethane, nitrobenzene, dimethyl sulfoxide, trifluoroacetic acid, hexfluoroisopropanol, o-chlorophenol, chloroform and toluene were added successively to each flask by syringe and the tubes were closed with ground glass stoppers. The flasks were allowed to stand for 72 hours at 25°C. The solid materials remaining after 72 hours were collected and the PMR spectrum of each filtrate was taken to detect the presence of soluble polymer. The PMR spectra showed solvent peaks, and in some cases small peaks corresponding to the protons in chlorodibromoacetaldehyde and the hydrate of this aldehyde. These were the only peaks observed. The acetone, toluene, chloroform and dichloromethane filtrates were evaporated and in every case a trace of solid remained which was the hydrate of chlorodibromoacetaldehyde. The dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol and nitrobenzene filtrates were

concentrated and then removed carefully at reduced pressure. No residues remained behind after complete solvent removal.

The solubility tests were repeated employing mixed solvent systems. Acetone/dichloromethane/toluene; dimethyl sulfoxide/benzene; nitro/benzene/o-dichlorobenzene. Polychloral samples were also tested for solubilities in these solvent combinations for comparison. No solid material, no poly (dibromochloroacetaldehyde) and no oligomers could be isolated from the filtrates after the polymers had been exposed for 72 hours to these solvent mixtures.

56. Solubility Tests for Chlorodibromoacetaldehyde-isocyanate copolymers.

In each of 10 dry Erlenmeyer flasks with ground glass joints were placed 1 gram of the solvent to be tested. The solvents acetone, dichloromethane, nitrobenzene, dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol, o-chlorophenol, chloroform, and toluene were added successively to each test tube by syringe and the tubes were closed with ground glass stoppers. The flasks were allowed to stand for 72 hours at 25°C. The solid materials remaining after 72 hours were collected and the PMR spectrum of each



filtrate was taken to detect the presence of soluble polymer. The PMR spectra showed solvent peaks. These were the only peaks observed. The acetone, toluene, chloroform and dichloromethane filtrates were evaporated and in every case no solid remained. The dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol and nitrobenzene filtrates were concentrated and then removed completed at reduced pressure. No residues remained behind after complete solvent removal.

The solubility tests were repeated employing mixed solvent systems: acetone/dichloromethane/toluene; dimethyl sulfoxide benzene; nitrobenzene-o-dichlorobenzene. Polychloral samples were also tested for solubilities in these solvent combinations for comparisons. No solid materials, neither polychloral nor chlorodibromoacetaldehyde copolymers could be isolated from the filtrates after the polymers had been exposed for 72 hours to these solvent mixtures.

57. Stabilization of Polychlorodibromoacetaldehyde by Treatment with  $\text{PCl}_5$ .

To a dry 125 ml. flask being slowly purged with dry nitrogen were added polychlorodibromoacetaldehyde (1.0 g) and  $\text{PCl}_5$  (15 ml. of a 1M solution in  $\text{CCl}_4$ ). A reflux

condenser was connected to the flask and the flask was heated to reflux with an oil bath for 2 hours. The flask was allowed to cool, the product was collected on a sintered funnel, rinsed with  $\text{CCl}_4$  (50 ml.) and dried under nitrogen (0.89 g, 89% yield). The infrared spectrum of this product could be superimposed on spectra for polychlorodibromoacetaldehyde. A TGA of this product indicated that the thermal stability was increased by this treatment.

58. Reaction of Polybromodichloroacetaldehyde with 2,4 Dinitrophenylhydrazine Solution.

Polybromodichloroacetaldehyde (0.10 g) and 2,4 dinitrophenylhydrazine (0.5 g in 10 ml methanol 2 ml  $\text{H}_2\text{O}$  and 0.5 ml concentrated  $\text{H}_2\text{SO}_4$ ) were added to an 8 inch test tube and the test tube was closed with a ground glass stopper. The mixture was allowed to stand at  $25^\circ\text{C}$  for 7 days. Methanol (10 ml) was added to the mixture and the solid material was collected on a sintered funnel, rinsed with methanol (50 ml.) and dried under nitrogen. The product (0.092 g, 92% recovered) had an infrared spectrum that could be superimposed on spectra for polydichlorobromoacetaldehyde. Very little attack occurred and no visible

changes were noticed during the 7 days in the reaction tube.

59. Reaction of KI with a Chlorodibromoacetaldehyde Polymer.

Polychlorodibromoacetaldehyde (1.0 g) and potassium iodide (1.0 g in 50 ml. of acetone) were allowed to stand in the dark at 25°C in a stoppered flask for 16 hours. The solid remaining was collected on a funnel rinsed with acetone (100 ml.) and dried under nitrogen. The product was soaked in acetone (50 ml.) and then collected and dried in a vacuum desiccator for 24 hours. An infrared spectrum of this product could be superimposed on previous polychlorodibromoacetaldehyde spectra.



## P. PURIFICATION AND POLYMERIZATION OF BROMAL

### 60. Purification of Bromal

A three neck 250 ml round bottom flask was equipped with a nitrogen inlet tube and a reflux condenser. The flask was purged with nitrogen for five minutes and then antimony trifluoride (5.0 g), bromal (50 ml) and a 3/4" Teflon covered stirring bar were added through the third neck with a funnel. A still head was placed in one neck and the flask was heated in an oil bath to 100°C. for two hours. The flask was then allowed to cool to room temperature and bromal was filtered under nitrogen pressure through a medium fritted funnel. It was then poured into a 250 ml round bottom flask (and 3.0 g of powdered  $P_2O_5$  was added) and distilled from the  $P_2O_5$  at 50 mm under nitrogen through an 8 inch Vigreux column. The first 5 ml of distillate were red and were discarded. After the distillate became colorless it was collected until 10 ml of liquid remained in the distillation flask. The bromal collected contained less than 0.1% impurities by volume according to analysis by gas chromatography, and was used immediately for the polymerization experiments. The best column for bromal



analysis by gas chromatography was a diisodecyl phthalate (36%) on chromosorb W and the optimum column temperature was 130°C. The infrared spectrum of pure bromal showed a carbonyl absorption at 1742  $\text{cm}^{-1}$  (neat), 1754  $\text{cm}^{-1}$  (in hexane, or 1765  $\text{cm}^{-1}$  (gas phase). The remainder of the spectrum could be superimposed on standard published infrared spectra for bromal.

61. Polymerization of Bromal with Lithium tert-Butoxide.

A 12 inch long (10 mm. I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (2.0 ml, 20 mmole) and lithium tertiary butoxide (0.67 ml of a 0.3 M solution in methyl cyclohexane 0.2 mmole, 1.0 mole percent) and toluene (0.4 ml) were added with a dry syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 pressure, and then placed in a -45°C for ten minutes. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice acetone bath at -78°C for 72 hours. This polymerization, like the polymerization of bromal with pyridine, gave a homogeneous gel.

The tube was allowed to warm to room temperature, cut into one inch sections. The sections containing the polymer were soaked in acetic anhydride (25 ml.) for 8 hours. The acetic anhydride was decanted into a small beaker. The product was broken up, with great difficulty, with a microspatula and the small pieces of polymer were soaked in acetone for 16 hours. After isolation and drying, polybromal was obtained as small colorless translucent granules (2.073 g, 37% yield). An infrared spectrum of this product could be superimposed on an infrared spectrum of the polybromal prepared by pyridine initiation. In a separate experiment, where lithium tertiary butoxide was used in a 0.3 mole percent concentration instead of a 1.0 mole percent concentration, polybromal was obtained in 6% yield. If the initiator and bromal were mixed in the sealed tube at 25°C very little polymer was isolated. At the higher temperature some side reaction took place.

## 62. Polymerization of Bromal with Pyridine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (4.0 ml., 40 mmole) was added

with a dry syringe. Pyridine (0.8 ml. of a 1M solution in toluene 0.8 mmole, 2 mole percent) was then added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken to mix the reactants thoroughly and was then placed in a dry ice/acetone bath at  $-78^{\circ}\text{C}$  for 72 hours. After cutting the tube into 1 inch sections the polymer was transferred to an Erlenmeyer flask containing acetic anhydride (40 ml.) and acetone (40 ml.), and stored in the refrigerator for 8 hours at  $-10^{\circ}\text{C}$ . The polymer was isolated soaked in acetone for 16 hours, collected on a M fritted funnel (10-15 u), and dried, Polybromal was obtained as small colorless translucent chunks (3.89 g, 47% yield). This experiment was repeated using 2.5 mol % pyridine 1.0 mole % pyridine, 5.0 mole % pyridine and 2.0 mole % pyridine again. The yields obtained were 46.3%, 44%, 42.6%, and 52%. In two experiments the initiator concentration was 0.5 mole percent but no polymer was isolated. A certain minimum initiator concentration was required for a successful polymerization of bromal with pyridine. If the diluent toluene was not present the bromal crystallized at

a temperature that was well above the polymerization threshold temperatures. If 1M methyl cyclohexane or n-hexane solutions of pyridine were used, the bromal crystallized out of solution and not polymerize. In addition, very little polymer was obtained if the order of addition above was reversed. If the pyridine was added before the toluene the initiator could not be dispersed evenly throughout the bromal. Large concentrations of pyridine in contact with bromal apparently caused a side reaction. Finally, it was absolutely necessary to use freshly distilled bromal in a tube sealed under vacuum for a successful polymerization.

An infrared spectrum of polybromal showed absorptions at  $2938\text{ cm}^{-1}$  (m) (C-H stretch);  $1358\text{ cm}^{-1}$  (w),  $1339\text{ cm}^{-1}$  (m),  $1300\text{ cm}^{-1}$  (s) (C-H bending);  $1048\text{ cm}^{-1}$  (vs),  $1021\text{ cm}^{-1}$  (s),  $910\text{ cm}^{-1}$  (vs),  $1086\text{ cm}^{-1}$  (vs) (C-O stretching),  $772\text{ cm}^{-1}$  (s),  $740\text{ cm}^{-1}$  (s),  $712\text{ cm}^{-1}$  (vs) (C-Br stretching),  $535\text{ cm}^{-1}$  (m).  
Anal. Calcd. for  $\text{C}_2\text{HBr}_3\text{O}$ : 8.59%; H, 0.36%; Br, 85.37%.  
Found: c, 8.85%, H, 0.42%, Br. 85.11%.

63. Polymerization of Bromal with Trifluoromethane Sulfonic Acid.

To a polymerization tube was added Bromal (8 ml, 78



mmol), dichloromethane (8 ml.) and trifluoromethanesulfonic acid (0.1 ml) at 25°C. The stopcock was closed and the polymerization tube was placed in a -78°C bath for two weeks. At the end of two weeks a white solid had collected at the bottom of the tube. The tube was removed from the cold bath and placed in a refrigerator at -22°C. for one additional week. No visible change took place during this week. The tube was removed from the refrigerator and opened. Hexane (5 ml) was added but no solid material precipitated. The solid product was collected, washed with cold acetone (30 ml.) and dried. Polybromal was obtained as a white powder (0.57 g, 3% yield). The infrared spectrum could be superimposed on previously described spectra for polybromal. No hydroxyl absorption was observed in the 3200-3600  $\text{cm}^{-1}$  region in a nujol mull of this sample.

## Q. COPOLYMERIZATION OF BROMAL

64. A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9, and freshly distilled p-methylphenylisocyanate (2.0 ml, 8 mmole) and toluene (0.3 ml) were added with a dry syringe. The tube was shaken and then pyridine (0.3 ml of a 1M solution in toluene 0.3 mmole, 2 mole %) was added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature; it was shaken and then placed in a dry ice/acetone bath at  $-78^{\circ}\text{C}$ . and was not disturbed. The tube was allowed to warm to room temperature, cut open; and a light yellow syrup was isolated and placed in acetone (15 ml.) in a 50 ml beaker. After 20 minutes stirring a light yellow precipitate had formed and some of the color was extracted by the acetone. Hexane (15 ml.) was added and a very slight amount of additional material separated out. The product was collected, washed with hexane (50 ml.) and dried. The product was extracted in acetone (20 ml.) for 12 hours, filtered and dried. The infrared spectrum of this polymer contained an absorption due to trapped p-methylphenylisocyanate and was further washed and finally

dried in the Abderhalden overnight at 0.1 mm. The bromal-p-methylphenylisocyanate copolymer was obtained as a light buff powder (2.95 g, 48% yield). An infrared spectrum (KBr) showed absorptions at  $2940\text{ cm}^{-1}$  (m) (C-H stretching);  $1730\text{ cm}^{-1}$  (m) (C-O stretching, urethane);  $1595\text{ cm}^{-1}$  (m),  $1504\text{ cm}^{-1}$  (s) (Phenyl);  $1370\text{ cm}^{-1}$  (w);  $1343\text{ cm}^{-1}$  (m),  $1305\text{ cm}^{-1}$  (s) (C-H bending);  $1100\text{ cm}^{-1}$  (vs),  $1061\text{ cm}^{-1}$  (vs),  $1040\text{ cm}^{-1}$  (s),  $950\text{ cm}^{-1}$  (vs) (C-O stretching);  $780\text{ cm}^{-1}$  (m),  $758\text{ cm}^{-1}$  (s),  $719\text{ cm}^{-1}$  (vs) (C-Br stretching),  $805\text{ cm}^{-1}$  (w) (parasubstituted phenyl). This experiment was repeated except that in this run the p-methylphenylisocyanate was not freshly distilled and the bromal had stood in the refrigerator for several hours after distillation. The yield of copolymer was 2.10 g, 34% before extraction with chloroform. Fractions of polymer rich in isocyanate content were removed by the chloroform extraction according to intensities of the urethane band in the infrared spectra. Anal. for N: Before chloroform extraction, 1.15%, after chloroform extraction 0.98%.

65. Copolymerization of Bromal with n-Butylisocyanate.

A 12 inch long (12 mm I.D.) pyrex tube was prepared according to Procedure #9.

To a mixture of freshly distilled bromal (5.0 ml, 50 mmole) and n-butylisocyanate (5.0 ml, 50 mmole) was added pyridine (0.05 ml, 0.6 mmole, 1.2 mole %) and toluene (2 ml) with a dry syringe. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature, shaken to mix the reactants and then placed in a dry ice-acetone bath at  $-78^{\circ}\text{C}$  for 72 hours and left in a quiescent state. The tube was removed from the bath and was allowed to warm to room temperature. The tube was opened and the reaction product, an inhomogeneous looking tough gel, was removed and placed in acetone (35 ml.). The solid material was collected on a M (10-15 u) fritted filter. No solid material separated out upon addition of hexane (10 ml.) to the filtrate. After drying, the bromal-n-butylisocyanate copolymer was obtained as light yellow granulates (8.76 g, 48.4%). The infrared spectrum showed absorptions at  $2940\text{ cm}^{-1}$  (m), (C-H stretch);  $1730\text{ cm}^{-1}$  (m) (C=O stretching, urethane);



1370  $\text{cm}^{-1}$  (w); 1343  $\text{cm}^{-1}$  (m), 1305  $\text{cm}^{-1}$  (s) (C-H bending); 1100  $\text{cm}^{-1}$  (vs), 1061  $\text{cm}^{-1}$  (vs), 1040  $\text{cm}^{-1}$  (s), 950  $\text{cm}^{-1}$  (vs) (C-O stretching); 789  $\text{cm}^{-1}$  (m), 758  $\text{cm}^{-1}$  (s), 719  $\text{cm}^{-1}$  (vs) (C-Br stretching). Anal. for N: 0.45%. This corresponds to about 7% isocyanate in the polymer.

66. Copolymerization of Bromal and Phenyl Isocyanate with Pyridine (10% isocyanate in feed).

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (2 ml., 20 mmole), phenylisocyanate (0.2 ml, 2 mmole) and pyridine (0.4 ml of 1M solution in toluene 0.4 mmole, 2 mole %) were added with dry syringes.

The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken and was then placed in a dry ice-acetone bath at  $-78^{\circ}\text{C}$  for 5 days. After 12 hours a gel had formed but the tube was allowed to remain at  $-78^{\circ}\text{C}$  to complete the reaction. The tube was allowed to warm to room temperature, opened and a red, hard gel was removed and placed in a 50 ml. beaker with acetone (20 ml). The

solid pieces of polymer were stirred; after 30 minutes, petroleum ether (15 ml.) was added, stirring was continued. No additional material separated out. The product was collected on a M fritted funnel (10-15 u) and dried. The bromal-phenylisocyanate copolymer was obtained as slightly buff-white cylinders (3.11 g, 53% yield). (In a separate experiment which was identical to this one except that 1 drop of pure pyridine was added directly to the monomer mixture, a 50.4% yield was obtained.) A considerable quantity of material precipitated from the acetone solution with petroleum ether. Both fractions were dried. The fraction which was initially soluble in acetone was no longer soluble in acetone after precipitation and solvent removal. Yield: 2.07 g, 38% insoluble, 0.65 g, 12.1% "soluble". The infrared spectrum showed absorptions at (for all three copolymers) 304 cm (w) (C-H stretching, aromatic); 2940 cm<sup>-1</sup> (m) (C-H stretching, acetal); 1730 cm<sup>-1</sup> (vs) (C=O stretching, urethane); 1610 cm<sup>-1</sup> (m), 1601 cm<sup>-1</sup> (m), 1522 cm<sup>-1</sup> (w), 1495 cm<sup>-1</sup> (s), 1490 cm<sup>-1</sup> (m), 1440 cm<sup>-1</sup> (w), 1419 cm<sup>-1</sup> (aromatic, phenyl absorptions); 1370 cm<sup>-1</sup> (w), 1350 cm<sup>-1</sup> (m), 1095 cm<sup>-1</sup> (vs), 1050 cm<sup>-1</sup> (vs), 940 cm<sup>-1</sup> (vs), 805

$\text{cm}^{-1}$  (w),  $782 \text{ cm}^{-1}$  (m),  $760 \text{ cm}^{-1}$  (s),  $721 \text{ cm}^{-1}$  (s),  $697 \text{ cm}^{-1}$  (s). Anal. for N: 0.77%. This corresponds to 9% isocyanate in the copolymer.

67. Preparation of Bromal-Phenylisocyanate. 1:1 Copolymer.

A 12 inch long (12 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled phenylisocyanate (3.1 ml., 3 mmole) and then freshly distilled bromal (3.0 ml., 3 mmole) was added by dry syringe. Pyridine (0.6 ml. of a 1.0 molar solution in toluene, 0.6 mmole or 3 mole percent) was then added carefully as a layer with minimal mixing. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the cooling bath and allowed to warm to room temperature, shaken thoroughly and then placed in a dry ice-Isopropyl alcohol bath at  $-78^{\circ}\text{C}$  for 96 hours. After 96 hours the tube was removed from the bath and was allowed to warm to room temperature. The tube was opened and a red wax was isolated and placed in acetone (30 ml.). The wax completely dissolved and gave a viscous solution. Hexane (75 ml.) was added to precipitate the polymer and the mixture

was stirred for 5 minutes. The product was collected on a fritted filter and dried. The phenylisocyanate-bromal 1:1 copolymer was obtained as a yellow powder (6.24 g, 74% yield). An infrared spectrum (KBr) showed absorptions at 3040  $\text{cm}^{-1}$  (aromatic C-H stretching), 2930  $\text{cm}^{-1}$  (C-H stretching acetal); 1740  $\text{cm}^{-1}$  (vs) (Carbonyl stretch), 1595  $\text{cm}^{-1}$  (m) (monosubstituted phenyl); 1495  $\text{cm}^{-1}$  (m) monosubstituted phenyl), 1372  $\text{cm}^{-1}$  (w), 1320  $\text{cm}^{-1}$  (s), 1270  $\text{cm}^{-1}$  (vs), 1245  $\text{cm}^{-1}$  (s), 1100  $\text{cm}^{-1}$  (s), 970-1005 (m, b), 800  $\text{cm}^{-1}$ ; (w), 750  $\text{cm}^{-1}$  (s), 1730  $\text{cm}^{-1}$  (s), 680  $\text{cm}^{-1}$  (vs). The PMR spectrum ( $\text{CDCl}_3$ ) shows a broad peak at 6.5 - 7.1 ( $\delta$  = TMS). Anal. Calcd. for  $\text{C}_8\text{H}_6\text{NO}_2$ : N, 3.42%; found, N, 3.61%, 3.02%.



## R. ATTEMPTED POLYMERIZATION OF BROMAL

68. Attempted Polymerization of Bromal with Triphenylphosphine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole) was added with a dry syringe; triphenylphosphine (0.4 ml. of a 0.3 M solution in cyclohexane, 0.12 mmole, 0.6 mole percent) was added and toluene (0.2 ml) was also added. The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature, shaken, and was then placed in a dry ice-Isopropyl alcohol bath for 72 hours. At the end of this time the tube was removed and inspected. No solid material was visible after an additional 72 hours at  $-78^{\circ}\text{C}$ .

The experiment was repeated with a 1 mole percent concentration of triphenylphosphine. But again no polymer was isolated.

69. Attempted Polymerization of Bromal with Triethyl-aluminum.

A 12 inch long (10 mm I.D.) pyrex tube was prepared

according to Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole) was added with a dry syringe followed by triethylaluminum (0.13 ml. of a 1.0 M solution in hexane, 0.12 mmole, 0.6 mole percent) was added and toluene (0.2 ml.). The tube was inserted in a liquid nitrogen bath, sealed at 0.1 mm pressure, and then allowed to come to room temperature. The tube was shaken and then placed in a dry ice-isopropyl alcohol bath for 72 hours. No solid material had precipitated nor could there be any material precipitated from the solution.

The experiment was repeated with a 1 mole percent concentration of triethylaluminum, but no polymer or other solid material was found.

70. Attempted Polymerization of Bromal with Tri-n-butylphosphine.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to the Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole), tri-n-butylphosphine (0.4 ml. of a 0.3 M solution in toluene, 0.12 mmole, 0.6 mole percent) and toluene (0.2 ml.) were added and the reactants mixed thoroughly. The tube sealed

at 0.1 mm pressure and was then placed in a dry ice-iso-propyl alcohol bath for 72 hours. No solid material was visible and no product could be isolated by precipitation from the liquid.

The experiment was repeated with a 1 mole percent concentration of tri-n-butyl-phosphine but no polymer was found.

71. Attempted Polymerization of Bromal with Antimony Pentachloride.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole) was added with a dry syringe (12 inch needle). Care was taken to prevent the aldehyde from contaminating the top half of the tube, antimony pentachloride (0.4 ml. of a 0.3 M solution in dichloromethane, 0.12 mmole, 0.6 mole percent) and dichloromethane (0.2 ml.) were sealed and placed for one week in a  $-78^{\circ}\text{C}$ . No solid material could be isolated.

72. Attempted Polymerization of Bromal with Phosphorous Pentachloride.

A 12 inch long (10 mm I.D.) pyrex tube was prepared

according to Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole) phosphorous pentachloride (0.4 ml. of a 0.3 M solution in dichloromethane, 0.12 mmole, 0.6 mole percent) and toluene (0.2 ml.) were sealed and placed in a  $-78^{\circ}\text{C}$  bath for one week. No solid material was isolated after that time.

73. Attempted Copolymerization of Bromal and Acrylonitrile.

A 12 inch long (10 mm I.D.) pyrex tube was prepared according to Procedure #9.

Freshly distilled bromal (2.0 ml., 20 mmole) and dry acrylonitrile (0.3 ml., 6 mmole) and pyridine (0.4 ml. of a 1M solution in toluene 0.4 mmole, 2 mole percent) were added by syringe and were sealed and placed for 72 hours in a  $-78^{\circ}\text{C}$  bath. A white powdery material was noticed in the tube. The product was removed from the tube was placed in acetone (20 ml.). The insoluble solid was collected by filtration, rinsed with more acetone (50 ml.), methanol (20 ml.), and Skelly F (20 ml.), and dried. An infrared spectrum of this solid could be superimposed on previous spectra for polybromal. No nitrile band was visible.



Evaporation of the filtrates from the workup yielded only bromal hydrate. Polybromal was obtained as a white powder (1.77 g, 31% yield).

74. Attempted Copolymerization of Bromal and Trioxane.

An 8 inch test tube was dried. Freshly recrystallized trioxane (3.0 g, 0.033 mole) was placed in the tube, followed by freshly distilled bromal (28 g, 0.1 mole) and antimony pentachloride (0.1 ml. of a 0.3 M solution in dichloromethane) was added with a dry syringe. The test tube was lowered into an oil bath of 35°C when reaction took place. After one hour the tube was removed from the oil bath and allowed to cool to room temperature. The tube was opened and dichloromethane (15 ml.) was added. The solid product was isolated and dried in a nitrogen stream. An infrared spectrum of the dry product could be superimposed on a spectrum of polyoxymethylene which was obtained (2.69 g, 88% yield) as a white powder.

The filtrate from the test tube was poured into Skelly F. No additional solid material was isolated upon attempted precipitation.

75. Attempted Copolymerization of Bromal and Chloral with  $\text{CF}_3\text{SO}_3\text{H}$ .

A 12 inch long (15 mm I.D. ) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chloral (8 ml., 80 mmole) bromal (8 ml. 80 mmole) and 1.6 ml. of  $\text{CF}_3\text{SO}_3\text{H}$  solution (1M solution of  $\text{CH}_3\text{SO}_3\text{H}$  in dichloromethane, 1.6 mmole 2.0 mole %) were added with dry syringes. The tube was inserted in a liquid nitrogen bath sealed at 0.1 mm, removed from the cooling bath and allowed to come to room temperature. The tube was shaken thoroughly and then placed in a dry-ice chlorobenzene/slush bath at  $-45^\circ\text{C}$  for 1 week. The tube was then warmed to room temperature and the solid product was collected on a fritted funnel, washed with acetone (30 ml.) and dried under nitrogen. The product was extracted with acetone for 24 hours in a Soxhlet apparatus, air dried, and dried in a vacuum desiccator for 24 hours. An infrared spectrum of this white powder (2.40 g, 15% yield) had an infrared spectrum which could be superimposed on previous spectra for polychloral. Analysis for Bromine indicated that this element was not present.

## S. CHARACTERIZATION OF BROMAL POLYMERIZATIONS

76. Visual Ceiling Temperature Determination for Bromal in Toluene with Pyridine.

Four six inch test tubes were washed in IN HCl, rinsed with distilled water four times and dried for 72 hours at 120°C. One tube was removed from the oven and quickly closed with a serum cap. A syringe needle (#17, 8" long) connected to a source of dry nitrogen was inserted through the serum cap and a second syringe (#17, 2" long) was also inserted as a nitrogen outlet. The test tube was purged with nitrogen for 10 minutes and then freshly distilled bromal (3.0 ml., 30 mmole) was added by dry syringe while the flow of dry nitrogen was maintained. The lower half of the test tube was then heated in an oil bath to 50°C. Toluene (2.7 ml.) and pyridine (0.3 ml. of a 1M solution in toluene 0.3 mmole, 1 mole %) were added by dry syringe. The tube was agitated and placed in an isopropyl alcohol bath at 25°C. The bath was allowed to cool at 2°C per minute while being stirred. Small pieces of dry ice were added while the bath was stirred rapidly. At 52°C a slight cloudiness was observed in the test tube. Addition of dry ice was continued until the temperature reached -75°C. The

test tube was removed from the cold bath and a self supporting gel was observed in the tube. The cloud point at  $-50^{\circ}\text{C}$  was recorded as the polymerization temperature of a 5 molar monomer concentration.

In the second test tube freshly distilled bromal (3.0 ml., 30 mmole) and pyridine (0.3 ml. of a 1M solution in toluene, 0.3 mmole, 1 mole percent) were added with dry syringes, were agitated and placed in an isopropyl alcohol bath at  $25^{\circ}\text{C}$ . The bath was cooled at  $2^{\circ}\text{C}$  per minute and stirred rapidly. At  $-37^{\circ}\text{C}$  a cloudiness was observed. Addition of dry ice was continued until the temperature reached  $-75^{\circ}\text{C}$ . The tube was removed from the bath and the tube was broken. An opaque plug of polymer was removed. The threshold temperature was recorded as  $-35^{\circ}\text{C}$  for a 9 molar solution of the aldehyde in toluene.

The experiment was repeated using exactly the same procedure. The threshold temperatures for a 6 M solution of monomer and a 7.5 M solution of monomer in toluene was determined to be  $-52^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .  $-43^{\circ}\text{C} \pm 5^{\circ}\text{C}$ . respectively. The tubes were opened and dichloromethane (15 ml.) was added. The solid products were isolated and dried in a



nitrogen stream. An infrared spectrum of each of the dry products could be superimposed on a spectrum of polybromal. The cloud temperatures were recorded and on a plot of  $1/T$  cloud vs  $\log [M]$  a 1 M ceiling temperature of  $-75^{\circ}\text{C} \pm 5^{\circ}\text{C}$  was determined by extrapolation.

77. Instrumental Ceiling Temperature Determination for Bromal in Toluene with Pyridine.

Four polymerization tubes were washed in 1N HCl, rinsed with distilled water four times and dried for 72 hours at  $120^{\circ}\text{C}$ . One tube was removed from the oven. A syringe needle (#17, 8" long) connected to a source of dry nitrogen was inserted. The test tube was purged with nitrogen for 10 minutes and then freshly distilled bromal (3.0 ml., 30 mmole) was added by dry syringe. The lower half of the test tube was cooled in liquid nitrogen. Toluene (2.7 ml.) and pyridine (0.3 ml. of a 3M solution in toluene 0.9 mmole, 3 mole %) were added by dry syringe. The tube was sealed, and placed in an isopropyl alcohol bath at  $25^{\circ}\text{C}$  and agitated. The bath was allowed to cool at  $2^{\circ}\text{C}$ . per minute while being stirred. Cold nitrogen gas was passed through a copper coil in the bath while the bath was

stirred rapidly. The intensity of a beam of light passing through the sample tube was recorded. The tube was removed from the cold bath and a self supporting gel was observed in the tube. The temperature at which the intensity of transmitted light began to decrease was recorded as polymerization temperature of 8.3 molar monomer concentration.

In the second tube freshly distilled bromal (3.0 ml., 30 mmole) and pyridine (1.5 ml. of a 0.6M solution in toluene 0.9 mmole, 3 mole percent) were added by dry syringe, the tube was sealed, agitated, and placed in an isopropyl alcohol bath at 25°C. The bath was cooled at 1°C per minute and stirred rapidly and the intensity of light transmitted was recorded. Stirring was halted during each reading. The tube was removed from the bath and the tube was broken. An opaque plug of polymer was removed. The threshold temperature was recorded as -41°C for a 6.7 molar solution of the aldehyde in toluene determined as the point where the transmitted light intensity began to decrease rapidly.

The experiment was repeated using exactly the same

procedure. The threshold temperatures for a 5.0 M solution of monomer in toluene was determined to be  $-50^{\circ}\text{C} \pm 3^{\circ}\text{C}$ .

78. Polymerization Rate of Bromal at  $-78^{\circ}\text{C}$  by NMR.

A NMR tube was prepared for the experiment according to a consistent cleaning procedure. The NMR tube was soaked in soap solution for 2 days, rinsed repeatedly with distilled water, washed with a dilute (1N)  $\text{HNO}_3$ , rinsed again repeatedly with distilled water and finally dried at  $120^{\circ}\text{C}$  for 72 hours. A 6 inch test tube was cleaned the same way and was dried at  $120^{\circ}\text{C}$  for 72 hours.

The test tube was removed from the oven and very quickly, a serum cap was placed over the open end, firmly attached with copper wire so that the serum cap would not accidentally slip off when a syringe needle was inserted through it. A syringe needle (#17, 5 inch) connected to a source of dry nitrogen was inserted through the serum cap and a second syringe needle (#17, 2 inch) was inserted as a nitrogen outlet. The test tube was clamped in a vertical position and the nitrogen flow was started. The tube was purged for 5 minutes and was heated with an air gun. It was allowed to cool to room temperature while a flow of



nitrogen was maintained, and was then lowered into an oil bath maintained at 50°C. Freshly distilled bromal (3 ml., 30 mmole) was added with a dry syringe through the serum cap and the temperature inside the test tube was allowed to reach 50°C in five minutes. Pyridine (0.6 ml. of a 1M solution in toluene, 2 mole percent, 0.6 mmole) was added with a dry syringe and the tube was agitated until mixing was complete. The NMR tube was removed from the oven, clamped in a vertical position and purged with dry nitrogen by means of a syringe needle (8 inch, #20) for 3 minutes. The NMR tube was placed in the 25°C oil bath to a depth of 3 inches. The initiated solution was then transferred from the test tube with a dry syringe to the NMR tube so that 2-1/2 inches of the NMR tube were filled with initiated monomer. The syringe needle connected to the nitrogen was removed and very quickly the NMR tube was closed with a pressure cap and the top of the NMR tube was wrapped with parafilm. The NMR tube was removed from the 25°C bath, wiped off and the zero time aldehyde proton ( $\delta = 8.9$ ) intensity was recorded. The methyl group resonance of the toluene was used as an internal standard. The NMR tube



was removed from the  $-78^{\circ}\text{C}$  bath after 2, 5, 10, 20, 40, 60, 120, and 360 minutes and the aldehyde peak intensity was determined together with the toluene methyl peak. The NMR tube was kept at the  $-78^{\circ}\text{C}$  for 72 hours and a final aldehyde peak intensity was determined to obtain a final conversion. The polymerization was essentially complete in 1 hour.

79. Vacuum Degradation of Polybromal Obtained by  $\text{Br}_3\text{CCHO}$  and Pyridine.

A 16 inch long pyrex tube (12 mm. I.D.) was bent into a U shape. One end of the U-tube was sealed and powdery polybromal (1.0 g) was placed in the U-tube. The tube was sealed on the other end at 0.1 mm pressure and the U-tube was placed in a liquid nitrogen bath and the other end, containing the polymer, in a silicone oil bath maintained at  $180^{\circ}\text{C}$ . for 30 minutes. At the end of this time a colorless solid had collected in the cold end of the U-tube. No residue or char remained in the hot end of the U-tube. The colorless solid was allowed to melt and the tube opened. A sample of the colorless liquid was drawn out with a 10 microleter syringe and immediately injected into a gas

chromatograph. The remainder of the colorless liquid was poured into a tared screw cap bottle (0.97 g or 97%). The analysis by gas chromatography (36% Di-isodecyl phthalate on chromasorb W) indicated that the colorless liquid was 97% monomeric bromal. An infrared spectrum of the colorless liquid could be nearly superimposed on previous spectra for the monomer.

Reproducible results were obtained when the polymer was ground in a mortar and pestle to a fine particle size prior to the experiment.

80. Stabilization of Polybromal by Treatment with  $\text{PCl}_5$ .

To a dry 125 ml. flask which was being slowly purged with dry nitrogen was added polybromal (3.0 g) and  $\text{PCl}_5$  (60 ml. of a 1M solution in  $\text{CCl}_4$ ). A reflux condenser was connected to the flask and the flask was heated to reflux with an oil bath for 2 hours. The flask was allowed to cool, the product was collected on a sintered funnel, rinsed with  $\text{CCl}_4$  (50 ml.) and dried under nitrogen (2.88 g, 96% yield). The product was washed with methanol (50 ml.) and then dried in a vacuum desiccator for 14 hours. An

infrared spectrum of the product could be superimposed on previous polybromal spectra. A TGA of this product indicated that the thermal stability was increased by this treatment.

#### 81. Solubility Tests for Bromal Homopolymers.

In each of 10 dry Erlenmeyer flasks with ground glass joints were placed 1 gram of the polymer to be tested. The solvents acetone, dichloromethane, nitrobenzene, dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol, o-chlorophenol, chloroform, and toluene were added successively to each test tube by syringe and the tubes were closed with ground glass stoppers. The flasks were allowed to stand for 72 hours at 25°C. The solid materials remaining after 72 hours were collected and the PMR spectrum of each filtrate was taken to detect the presence of soluble polymer. The PMR spectra showed solvent peaks, and in some cases small peaks corresponding to the proton in bromal and the hydrate of this aldehyde. These were the only peaks observed. The acetone, toluene, chloroform and dichloromethane filtrates were evaporated and in every case a trace

of solid remained which was the hydrate of bromal. The dimethyl sulfoxide, trifluoroacetic acid, hexafluoroisopropanol and nitrobenzene filtrates were concentrated and then removed completely at reduced pressure. No residue remained behind after complete solvent removal.

The solubility tests were repeated employing mixed solvent systems: acetone/dichloromethane/toluene; dimethyl sulfoxide/benzene; nitrobenzene - o-dichlorobenzene. Polychloral samples were also tested for solubilities in these solvent combinations for comparison. No solid material, neither polychloral nor polybromal could be isolated from the filtrates after the polymers had been exposed for 72 hours to these solvent mixtures.



product was washed with petroleum ether (200 ml.), removed from the filter and soaked in petroleum ether (200 ml.) for 24 hours, collected on a sintered glass funnel and air dried. The product was obtained as a fine white powder (2.09 g, 41% yield). The filtrates were evaporated and the solid residue isolated was identified as aldehyde hydrate. No polychloral and no oligomers of DCBA were detected. The fine white powder was tested for solubility in 10 solvents according to the procedure described in Experiment #36. This powder was insoluble in all solvents including DMSO. The o-chlorophenol severely swelled the powder and formed a paste which was a suspension and not a solution. The infrared spectrum of the product could be superimposed on previous spectra for polybromodichloroacetaldehyde.

84. Reaction of Chloral and Epichlorohydrin (4,5).

A large test tube (50 ccm.) which was flamed out and cooled under dry nitrogen was fitted with a serum cap through which two hypodermic needles were inserted. One of them was connected to the nitrogen line and was long

enough to reach to the bottom of the test tube, the other served as a nitrogen exit. The test tube was flushed with nitrogen and is then immersed in an oil bath at 70°C.

Freshly distilled chloral (10 ml., 0.1 mole) and epichlorohydrin (1.0 ml., 0.1 mole) were added through the serum cap with dry syringes.

After five minutes the temperature of the monomers reached the oil bath temperature and 0.2 ml. of a triphenylphosphine solution (1.0 molar in toluene) was injected with a hypodermic syringe. The slightly red solution was shaken until a homogeneous solution was obtained.

The initiated monomers were transferred with a warm hypodermic syringe into an assembly which consisted of two glass plates separated by a 0.1 mm. spacer (LYCRA). The assembly was filled from the top with initiated monomer and immediately immersed into an ice water bath and held in

the bath at 0° for 1 hour. The plates were separated, the polymer film was removed, rinsed with acetone and dried under reduced pressure at 100°C for 12 hours. The yield of product was 83% and was a clear tough film. An infrared spectrum (film) showed absorptions at 3030 cm<sup>-1</sup> (m) (C-H stretch); 3000 cm<sup>-1</sup> (w); 2945 cm<sup>-1</sup> (m) (C-H stretch); 1461 cm<sup>-1</sup> (w); 1420 cm<sup>-1</sup> (s); 1385 cm<sup>-1</sup> (w); 1360 cm<sup>-1</sup> (m) (E-H bending); 1325 cm<sup>-1</sup> (s) (C-H bending); 1181 cm<sup>-1</sup> (s); 1163 cm<sup>-1</sup> (m); 1122 cm<sup>-1</sup> (vs) (C-O stretching); 1085 cm<sup>-1</sup> (vs) (C-O stretching); 1070 cm<sup>-1</sup> (vs) (C-O stretching); 1028 cm<sup>-1</sup> (m); 975 cm<sup>-1</sup> (vs) (C-O stretching); 842 cm<sup>-1</sup> (vs) (C-C stretching and C-Cl stretching); 830 cm<sup>-1</sup> (vs) (C-C and C-Cl stretching); 745 cm<sup>-1</sup> (m); 700 cm<sup>-1</sup> (vs); 680 cm<sup>-1</sup> (s); 646 cm<sup>-1</sup> (vs).

85. Degradation of Polychloral by Piperidine in Dichloromethane.

A section of a polychloral film (1.716 g) was covered with dichloromethane (50 ml.) and piperidine (0.1 ml.) in a stoppered flask. At the end of 12 hours the film was removed, rinsed with CH<sub>2</sub>Cl<sub>2</sub> (50 ml.) and dried in an Aberralden at reduced pressure for 16 hours until a constant

weight of 0.858 grams was recorded. The film was treated again with piperidine (0.1 ml.) and dichloromethane (50 ml.) for 12 hours, rinsed with  $\text{CH}_2\text{Cl}_2$ , and dried to a constant weight of 0.850 g. The percent weight loss for this sample prepared with pyridine initiation was 50.3%. A similar degradation experiment on a polychloral sample prepared with triphenylphosphine initiation indicated at 49.3% loss of weight. A sample of polychloral prepared with  $\text{H}_2\text{SO}_4$  initiation showed a 77% loss in weight after 12 hours exposure to the piperidine solution.

86. The Reaction of Chlorodibromoacetaldehyde with Triethyl Aluminum.

A 12 inch long (10 mm. I.D.) pyrex tube was prepared as described in Experiment #9.

Freshly distilled chlorodibromoacetaldehyde (2.0 ml., 2 mmole) triethyl aluminum (0.1 ml. of a 1M solution in hexane, 0.1 mmole or 0.5 mole percent) and methyl cyclohexane (0.5 ml.) were added with dry syringes into this tube. The tube was inserted into a liquid nitrogen bath, sealed at 0.1 mm pressure, removed from the bath for 1 minute, and then placed in a  $-45^\circ\text{C}$  bath for 5 minutes.



The tube was removed from the bath, shaken, and quickly replaced in the bath. The tube was kept in the bath at  $-45^{\circ}\text{C}$  for 24 hours and was inspected. A small quantity of white material was visible at the top of the liquid. After an additional 48 hours in the  $-45^{\circ}\text{C}$  bath the tube was allowed to warm to room temperature. A white solid was present and no liquid monomer was visible. The tube was opened and was cut into sections. A tough porcelainlike solid was removed and divided into two parts. The first part was placed in hexane (25 ml) and stirred for 15 minutes. The solid was collected and dried. The hexane was evaporated and gave small column shaped colorless crystals which had a sharp melting point at  $53^{\circ}\text{-}54^{\circ}\text{C}$ .

The second part was dissolved in toluene (25 ml.) and was precipitated with hexane (30 ml.) and was stirred for ten minutes. The crystals were collected and dried. They had a melting point of  $53^{\circ}\text{-}54^{\circ}\text{C}$ . This compound proved to be 2,2-dibromo-2-chloroethyl-dibromochloroacetate, as colorless needles (4.28 g, 94% yield) m.p.  $53^{\circ}\text{-}54^{\circ}\text{C}$ . The infrared spectrum (KBr) showed absorptions at  $2955\text{ cm}^{-1}$  (m) (C-H stretch),  $1758\text{ cm}^{-1}$  (vs) (C=O stretch),  $1358\text{ cm}^{-1}$

(m),  $1260\text{ cm}^{-1}$  (s),  $1199\text{ cm}^{-1}$  (vs) (C-O stretch),  $1090\text{ cm}^{-1}$  (m),  $1004\text{ cm}^{-1}$  (s),  $900\text{ cm}^{-1}$  (w),  $800\text{-}815\text{ cm}^{-1}$  (s),  $758\text{ cm}^{-1}$  (w),  $732\text{ cm}^{-1}$  (m),  $673\text{ cm}^{-1}$  (m). Anal. Calcd. for  $\text{C}_4\text{H}_2\text{Br}_4\text{Cl}_2\text{O}_2$ : C, 10.17%; H, 0.42%; Cl, 15.01%; Br, 67.66%. Found, C, 10.02%; H, 0.65%; Cl, 14.70%; Br, 67.10%. A PMR spectrum showed: 5.0 PPM singlet ( $\delta$  TMS).

87. The Reaction of Chloral, Pivalolactone and Tributylphosphine.

The procedure for the reaction of chloral and pivalolactone copolymer was essentially the same as a preparation of the chloral homopolymer. A dry test tube, closed with a serum cap, was filled with 10 ml (15 gm., 0.1 moles) of freshly distilled chloral and 10 ml. of freshly distilled pivalolactone phenyl isocyanate. The mixture was heated in an oil bath at  $70^\circ\text{C}$  until the temperature of the mixture reached the oil bath temperature, 0.2 ml. of a molar solution of tributylphosphine in benzene was added with a hypodermic syringe. The initiated comonomer mixture was agitated and then cooled to  $0^\circ\text{C}$  in an ice water bath for 1 hour. The tube was opened and a plug of product was taped out. The plug was extracted for 24 hours in acetone

in soxhlet extractor and dried at reduced pressure yield at 18.76% g. An infrared spectrum showed absorptions at: 2980  $\text{cm}^{-1}$  (m), 2950  $\text{cm}^{-1}$  (m), 2895  $\text{cm}^{-1}$  (w), 1723  $\text{cm}^{-1}$  (vs) 1477  $\text{cm}^{-1}$  (m), 1382  $\text{cm}^{-1}$  (m), 1359  $\text{cm}^{-1}$  (s), 1320  $\text{cm}^{-1}$  (vs) 1260  $\text{cm}^{-1}$  (m), 1228  $\text{cm}^{-1}$  (s, b), 1183  $\text{cm}^{-1}$  (s), 1160  $\text{cm}^{-1}$  (s), 1122  $\text{cm}^{-1}$  (vs), 1068  $\text{cm}^{-1}$  (vs), 1083  $\text{cm}^{-1}$  (vs), 1030  $\text{cm}^{-1}$  (m), 968  $\text{cm}^{-1}$  (s, b), 858  $\text{cm}^{-1}$  (vs), 840  $\text{cm}^{-1}$  (vs), 803  $\text{cm}^{-1}$  (vs), 780  $\text{cm}^{-1}$  (m), 738  $\text{cm}^{-1}$  (w), 680  $\text{cm}^{-1}$  (m).  
Anal. for C1: C1 = 42.86%.

## RESULTS AND DISCUSSION



## PURPOSE

This work is undertaken to prepare polymer grade bromodichloroacetaldehyde and chlorodibromoacetaldehyde, to develop techniques for the polymerization of these two aldehydes, to find new techniques for the purification and possible polymerization of bromal itself, and to study the influence of the side group size on the stereoregularity, thermal stability, solubility, crystallinity, morphology and transitions of the polymers obtained.

This work is also undertaken to prepare copolymers of bromodichloroacetaldehyde, chlorodibromoacetaldehyde, and bromal with chloral, with isocyanates and with other monomers to study the influence of comonomer content on the chemical and physical properties of the copolymers obtained. Polychloral homopolymers and copolymers will be prepared as standards for comparison of polymer properties.

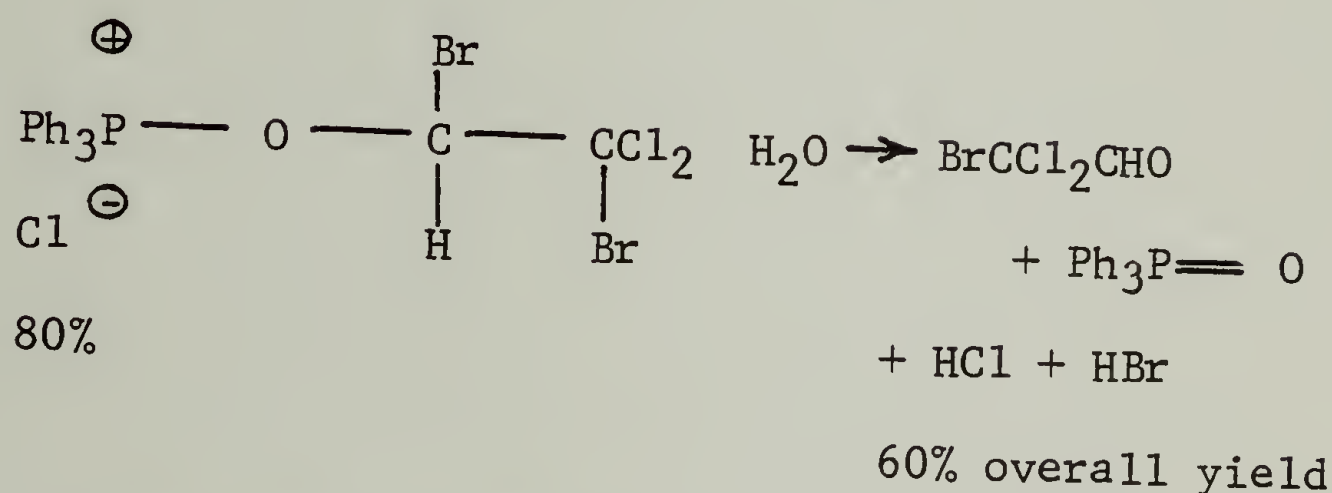
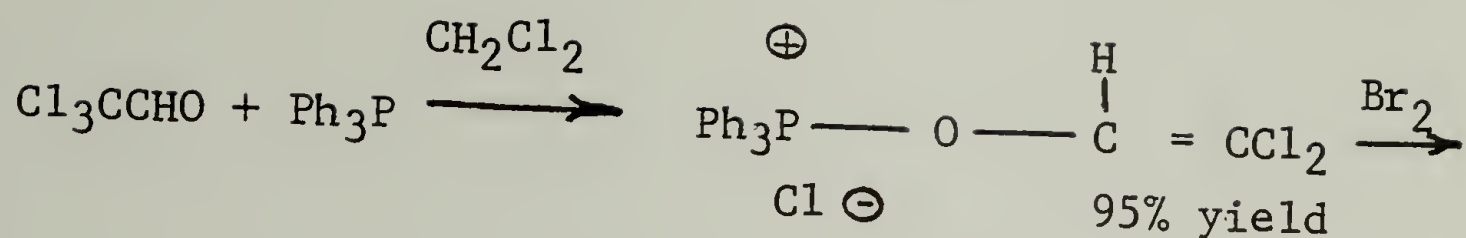
## MONOMER SYNTHESIS AND PURIFICATION

## 1. Bromodichloroacetaldehyde (NDCA)

BDCA was successfully synthesized by two methods. The first method consisted of a three step synthesis starting with the reaction of chloral with triphenylphosphine. The final yield of aldehyde obtained by this method was 60%. The second method was a bromination of dichloroacetaldehyde diethyl acetal. This second method was much inferior in yield of pure polymerization of grade monomer. Four other methods for the synthesis of BDCA were attempted several times but were not successful. The preparation of BDCA from triphenylphosphine and chloral was the only procedure actually used for the production of pure aldehyde for the polymerization experiments in this work.

Synthesis of BDCA from Chloral and Triphenyl Phosphine

BDCA was synthesized by a Perkow reaction from  $\text{Ph}_3\text{P}$  and chloral, a bromination, and a hydrolysis which was similar to the method of Hoffman and Diehr.<sup>(66)</sup> The reaction sequence produced pure aldehyde in an overall repeatable yield of 60%.



This reaction sequence was reported in a communication with no experimental details and although the sequence was reproducible the final yield of pure BDCA was poor unless several precautions were taken. We carried out this synthesis many times before the optimum experimental conditions were determined.

1. Unless moisture was excluded during the first two steps the phosphonium salts decomposed and the desired products were not obtained. The chloral had to be freshly distilled and all solvents rigorously dried, the reaction flask and addition funnel were flamed out and maintained under nitrogen during the first two steps.

2. The rate of addition and the rate of stirring were both important. Unless the chloral was added dropwise to the rapidly stirred triphenylphosphine solution the chloral accumulated and polychloral, rather than the phosphonium salt, was formed. Unless the bromine was added slowly in the second step so that the red color was discharged, a side reaction took place and the yield of the dibrominated phosphonium salt was considerably less. A good solvent for these phosphonium salts allowed better mixing and prevented accumulations of chloral in step one and bromine in step two. Dichloromethane was found to be superior to ether and many other solvents which did not completely dissolve the salts.

3. A solvent which was completely miscible with water and which partially dissolved the phosphonium salt was required for complete hydrolysis in step three. Dichloromethane and other solvents such as chloroform and carbon tetrachloride were not satisfactory because hydrolysis even in the presence of excess water was incomplete after several hours of refluxing.

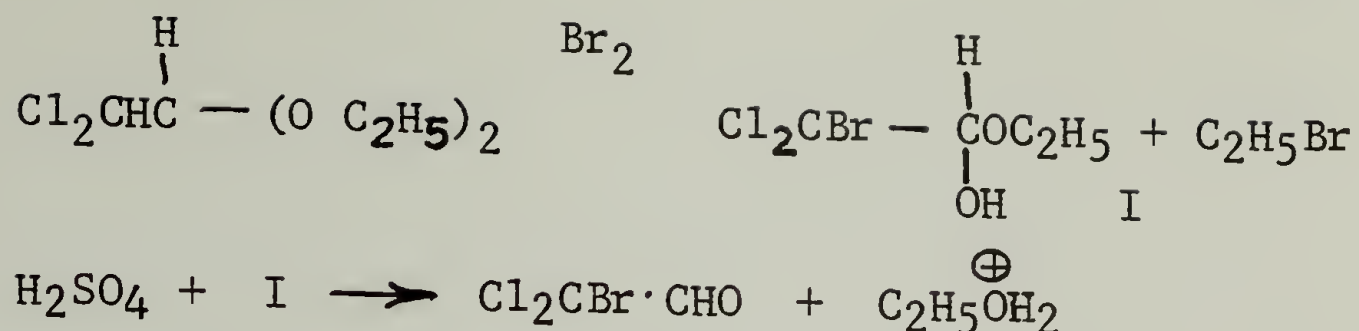


4. The greatest difficulty involved the separation of the BDCA from the product mixture in step three. It was necessary first to remove all HCl and HBr by refluxing the solution for several hours and then to separate the aldehyde from the triphenylphosphine oxide. In most solvents the hydrolysis of the phosphonium salt yield a gum of triphenylphosphine oxide. Great difficulties were encountered in separating the aldehyde from this gum. Dioxane, however, was found to be an excellent solvent. Triphenylphosphine oxide did not form a gum in dioxane and BDCA could be cleanly separated.

The aldehyde was separated from the dioxane on a spinning band column after refluxing for one hour over  $P_2O_5$ . The BDCA was then distilled twice from phosphorous pentoxide.

#### Synthesis of BDCA from Dichloroacetaldehyde Diethylacetal

An apparently simpler synthesis of BDCA from an acetal and bromine was much inferior.



The overall yield of aldehyde in this sequence was about 30%.

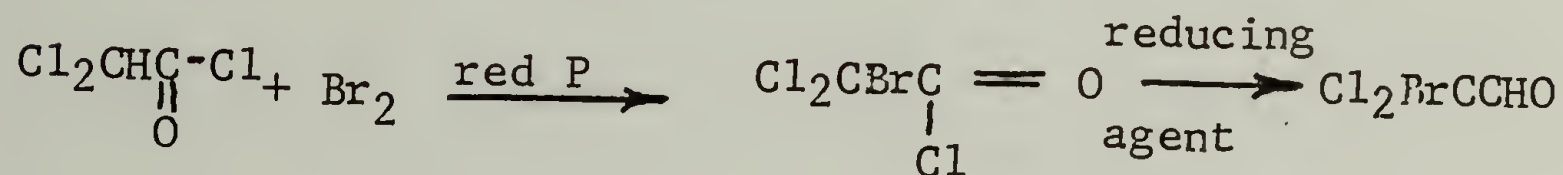
The bromine was added dropwise to a stirred solution of dichloroacetaldehyde diethylacetal at 100°C under a nitrogen atmosphere at a rate that just allowed the red color to be discharged. More rapid addition led to the formation of side products. The progress of the reaction was followed by NMR analysis of samples.

In the second step bromodichloroacetaldehyde monoethyl acetal was decomposed to BDCA in the presence of excess cold sulfuric acid. The aldehyde was separated from the acid after five minutes and was treated with  $\text{CaCO}_3$  since the aldehyde formed side products. When the aldehyde stood in a stoppered flask at room temperature without being treated with  $\text{CaCO}_3$  a solid polymer formed within a few hours. The aldehyde was purified by repeated distillation from powdered phosphorous pentoxide and then distillation on a spinning band column. In spite of the

repeated distillation several minor undesirable impurities always remained in the aldehyde.

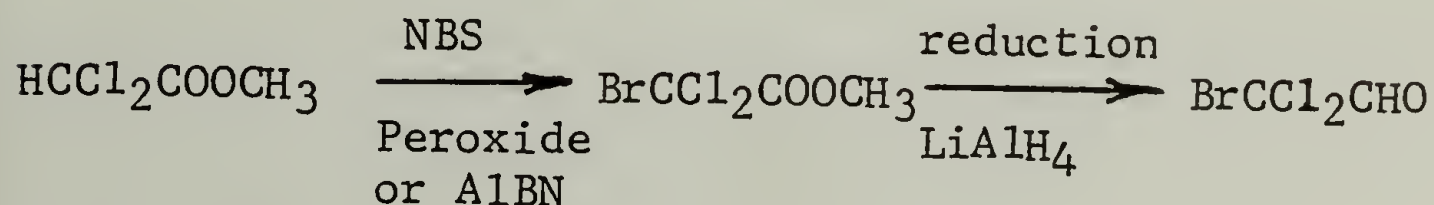
C. Attempted Synthesis of BDCA from Dichloroacetyl Chloride via the Hill-Volkard-Zelinsky

Aliphatic carboxylic acid chlorides will react with bromine in the presence of red phosphorous to form -bromocarboxylic acids. The following sequence of reactions was considered for an alternative synthesis of bromodichloroacetaldehyde. Bromine, dichloroacetyl chloride and red phosphorous did not react to form bromodichloroacetyl chloride at 100°-110°C.



D. Attempted Synthesis of BDCA by Radical Bromination

The following two step synthesis of BDCA from methyl-dichloroacetate was attempted.



In one experiment N-bromosuccinimide was reacted with  $\text{HCCl}_2\text{COOCH}_3$  and in the other experiment molecular bromine

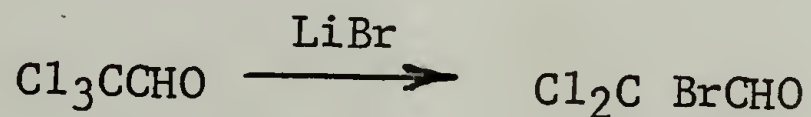
was used. After prolonged heating of the ester in the presence of benzoyl peroxide at reflux, under nitrogen, no reaction was observed. Perhaps the benzoyl peroxide was not able to abstract a hydrogen radical from the carbon atom of the ester. An analysis of the reaction mixtures revealed that the ester had not reacted. Azobisisobutyronitrile was substituted for the benzoyl peroxide as a bromination catalyst. Methyl dichloroacetate failed to react with bromine in the presence of AlBN.

E. Attempted Synthesis of BDCA from Chloral and Lithium Bromide

Alkanes monosubstituted with a halogen can be made to undergo a halogen exchange in the presence of certain alkali metal halides. (146)



An attempt was made to apply this type of reaction to chloral.



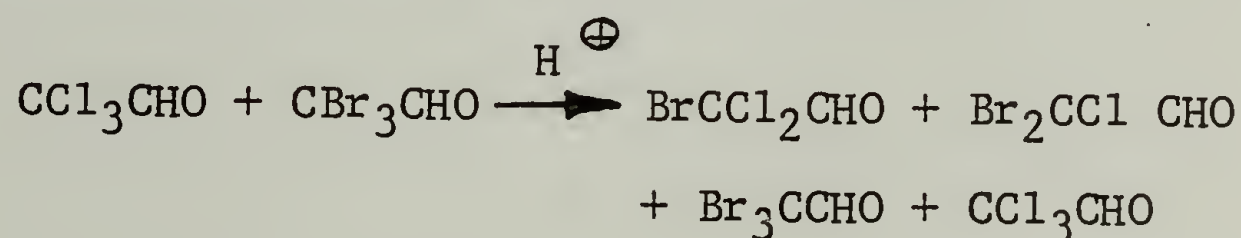
Chloral was refluxed over lithium bromide for twenty-



four hours under nitrogen but no reaction was observed according to an analysis of the reaction products by gas chromatography and NMR. Sodium bromide and potassium bromide were also used under similar reaction conditions but no halogen exchange was observed.

F. Attempted Synthesis of BDCA from Chloral and Bromal

The compounds 1,2-dichloroethane and 1,2-dibromoethane when mixed together were reported to form an equilibrium mixture of 25% 1,2-dichloroethane, 25%, 1,2-dibromoethane, and 50% 1,2-bromo ethane.<sup>(146)</sup> An attempt was made to exchange halogens between chloral and bromal as illustrated in the following reaction:



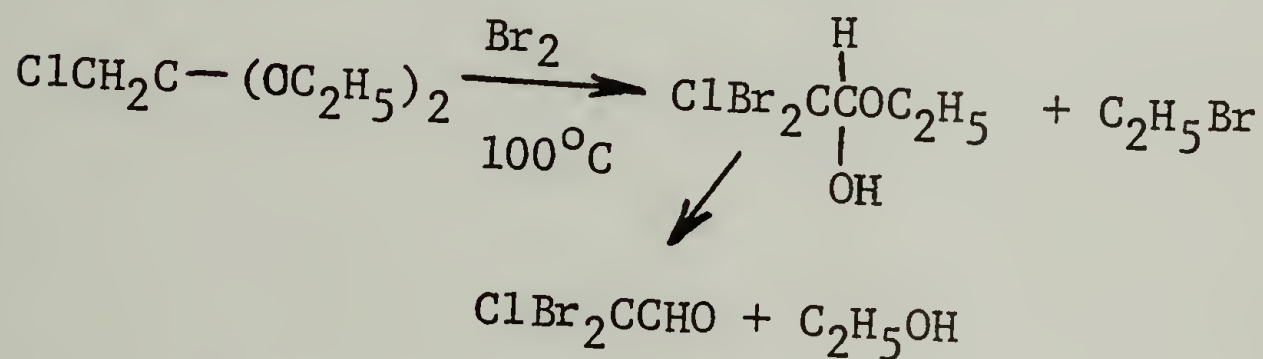
In the first experiment chloral and bromal were allowed to stand in a stoppered flask for three weeks. An analysis of the reaction mixture after this time, by gas chromatography, revealed that no reaction had taken place. In the second experiment the two aldehydes were exposed to sunlight in a polyethylene bottle and in a closed

Erlenmeyer flask. The analysis by gas chromatography revealed that only chloral and bromal were present but some red color formed during the solar irradiation.

## 2. Chlorodibromoacetaldehyde (CDBA)

### Synthesis from Chloroacetaldehyde ethylacetal and Bromine

CDBA was obtained in a 50% overall yield from chloroacetaldehydediethyl acetal and bromine.



Bromine was added to rapidly stirred acetal at a rate that just allowed the bromine color to be discharged. Chlorodibromoacetaldehyde mono-ethyl acetal was decomposed thermally at  $150^\circ\text{C}$  to give CDBA and ethanol. The ethanol was separated and collected during decomposition CDBA was distilled at  $150^\circ\text{C}$  at 100 mm pressure and a nearly pure product was obtained. The decomposition of the acetal and separation of ethanol from CDBA was possible without the use of  $\text{H}_2\text{SO}_4$ . After the ethanol and CDBA were separated,

of the distillate was discarded and only the middle cut, a colorless liquid, was used for the polymerization experiments. Analysis by gas chromatography revealed that the bromal contained less than 0.1% total impurities.

### C. Monomer Characterization

The two monomers BDCA and CDBA were characterized by elemental analysis, infrared spectra, nuclear magnetic resonance spectra and by their physical constants. Each of these characterization methods yields facts about these monomers that were used in some of the conclusions of this work. Chloral and bromal were also characterized by the above methods and the four monomers are compared below.

#### 1. Elemental Analysis

The chloral and bromal were commercial samples and were used as standards for the elemental analyses. The halogen analysis for chlorine and bromine in bromal, chloral, bromodichloroacetaldehyde and CDBA was difficult and were low at first. Satisfactory analyses for chlorine, bromine, carbon and hydrogen were obtained and these analyses are shown in Table 1 below.

the aldehyde was further purified on a spinning band column followed by distillation from powdered phosphorous pentoxide. An analysis by gas chromatography on polymerization grade monomer is shown in Appendix 3.

### 3. Purification of Bromal

A commercial sample of bromal was 99% pure according to analysis by gas chromatography. It had a red color which was only partially discharged by cyclohexene. A second red impurity was present. This red color persisted in the monomer even after it had been distilled several times from powdered phosphorous pentoxide. A purification scheme was devised to remove the remaining impurities and the color.

In the first step of the purification bromal was heated over antimony trifluoride at 80-100°C for one hour under dry nitrogen. The red color vanished and analysis by gas chromatography of the bromal revealed that three impurity peaks present in the unpurified bromal were nearly absent. Two of the three peaks were almost entirely missing. The aldehyde was distilled from  $P_2O_5$ . The first part



TABLE 1  
ELEMENTAL ANALYSES FOR MONOMERS

$\text{Cl}_2\text{CBr} \cdot \text{CHO}$			$\text{Br}_2\text{CCl} \cdot \text{CHO}$		
	Theory	Found		Theory	Found
Cl	36.96	36.72	Cl	15.01	15.00
Br	41.65	41.34	Br	67.66	67.28
C	12.52	12.24	C	10.17	10.38
H	0.53	0.66	H	0.42	0.69

Halogen analyses in these compounds containing a very high percent halogen by weight were sometimes low because they were difficult to burn. Incomplete combustion even in the presence of a pure oxygen atmosphere was often observed during the analysis. Analysis for chlorine in the presence of bromine was difficult because one halogen interfered with the determination of the other halogen. Monomer had to be freshly purified by distillation immediately prior to analysis for satisfactory results.

## 2. Derivatives

A 2,4-dinitrophenylhydrazone of BDCA was prepared in dimethylformamide. The method as described in the literature<sup>(147)</sup> for the preparation of 2,4 dinitrophenylhydrazones

was unsatisfactory for the preparation of a 2,4-dinitro-phenylhydrazone of BDCA. The literature method yielded a high melting compound containing no halogen but much more nitrogen than theory. In this work, dimethylformamide, acidified with HCl or  $\text{H}_2\text{SO}_4$ , was used as the solvent for the preparation of the 2,4-dinitrophenylhydrazone instead of water, ethanol and  $\text{H}_2\text{SO}_4$ . A yellow hydrazone was obtained in good yield and melting point was  $150^\circ\text{C}$ . An infrared spectrum is shown in Appendix 1.

Several attempts were made to prepare a 2,4-dinitro-phenylhydrazone of CDBA by various methods. A stable derivative was not isolated. Also, oximes of these two aldehydes appeared to be too unstable and too difficult to purify.

### Physical Constants

The values obtained for the boiling points and densities of chloral BDCA, CDBA and bromal are given in Table 2. (see page 193)

The boiling points and the densities of chloral, BDCA, CDBA and bromal increase approximately linearly with increasing bromine substitution. The melting points of these

TABLE 2  
BOILING POINTS AND DENSITIES OF MONOMERS

	Boiling point 760 mm	Density 25°C
$\text{Cl}_3\text{CCHO}$	97.75	1.45
$\text{Cl}_2\text{CBrCHO}$	127	1.87
$\text{Br}_2\text{CCl-CHO}$	148	2.27
$\text{Br}_3\text{C-CHO}$	174	2.73

compounds differ widely. Chloral melts at  $-57.5^\circ$  (60) while BDCA with its unsymmetrical substitution on the -carbon, melted at about  $-70^\circ\text{C}$  and melting points increased with increasing bromine substitutions.

#### 4. Nuclear Magnetic Resonance Spectra

The proton NMR spectra of the four haloaldehydes show a sharp singlet for each monomer. The values of the chemical shift are given in Table 3. (see p. 194) The aldehyde proton becomes increasingly shielded with increasing bromine substitution. With increasing bromine substitution more highly polarizable groups are present next to the aldehyde proton. The electrons would more effectively shield the

aldehyde proton in bromal than in chloral.

TABLE 3

## PMR CHEMICAL SHIFTS FOR MONOMERS

	$\delta_{\text{TMS}}$ (neat)
$\text{CCl}_3\text{CHO}$	8.95
$\text{Cl}_2\text{CBrCHO}$	8.85
$\text{Br}_2\text{C ClCHO}$	8.70
$\text{Br}_3\text{CCHO}$	8.45

The chemical shifts observed in the  $^{13}\text{Cl}_2\text{NMR}$  spectra of the four haloaldehydes are given in Table 4.

TABLE 4

 $^{13}\text{C}$  CHEMICAL SHIFTS FOR MONOMERS  
(Downfield from TMS in PPM, neat)

	$\text{C=O}$	$\text{CX}_3$
$\text{Cl}_3\text{C} \cdot \text{CHO}$	175.3	93.7
$\text{Cl}_2\text{C} \cdot \text{BrCHO}$	176.7	79.4
$\text{Br}_2\text{C} \cdot \text{Cl} \cdot \text{CHO}$	176.3	63.5
$\text{Br}_3\text{C} \cdot \text{CHO}$	176.9	45.5

The data in Table 4 indicate that the chemical shift of the carbonyl carbon is nearly constant in all four aldehydes even though the substituent groups differ considerably in their ability to withdraw electrons. The charge



density on the carbonyl carbon appears to be quite constant. The chemical shift of the carbon substituted with the halogens shows a trend with increasing bromine substitution. This type of trend has been observed in halogen substituted methanes.<sup>(148)</sup> The most important conclusion is that the chemical shift of the carbonyl carbon is not greatly influenced by the electronegativity of the substituent group in these aldehydes.

#### 5. Infrared Spectra

The infrared spectra of BDCA and CDBA are shown in Appendix 1. These spectra are very similar to published infrared spectra of chloral and bromal except in the region of  $900\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  where the carbon halogen bond stretch is generally observed.

Careful measurements were made to determine the exact location of the carbonyl band in the infrared mixtures for all four compounds. The carbonyl stretch frequencies were determined in the gas phase, in n-hexane, and neat for each aldehyde. The data are presented in Table 5.

TABLE 5

ALDEHYDE CARBONYL INFRARED STRETCHING ASSIGNMENTS  
( $\text{cm}^{-1}$ )

	gas	hexane	neat
$\text{Cl}_3\text{CCHO}$	1777	1768	1760
$\text{Cl}_2\text{CBr CHO}$	1774	1763	1754
$\text{Br}_2\text{C ClCHO}$	1768	1758	1750
$\text{Br}_3\text{CCHO}$	1765	1754	1742

The carbonyl stretching frequency linearly decreased with increasing bromine substitution. The carbon oxygen double bond decreases in polarity and decreases in double bond character with increasing bromine substitution. Bromine is less electron withdrawing than chlorine and substitution of bromine for chlorine stabilizes the resonance.



In the case of bromal the charge separated form is more important than in chloral and the carbon-oxygen bond in bromal has more single bond character. The polarities of the carbonyl groups in the four haloaldehydes influence their reactivities toward nucleophiles.

# D. Homopolymerization of CDBA, BDCA, and Bromal

All these monomers, bromal, CDBA and BDCA, polymerized in the presence of anions and certain acids to form substitute polyoxymethylenes with structures closely resembling the structure of polychloral.

## 1. Polymerization of BDCA

BDCA polymerized in the presence of a wide variety of initiators. Both anions and certain acids were effective initiators. The initiators, reaction conditions and yields are described in Table 7.

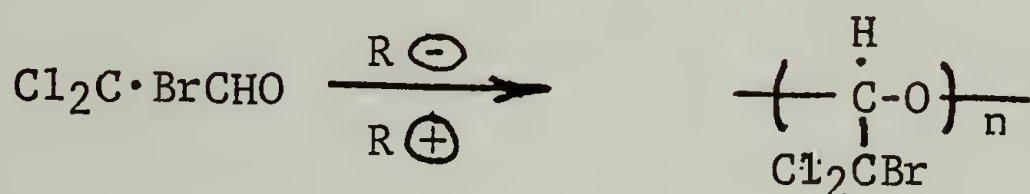


TABLE 7

Bulk Polymerization of  $\text{Cl}_2\text{C}\cdot\text{BrCHO}$  Reaction Temperature  $-30^\circ\text{C}$ . Initiator Concentration 2 Mole Percent

Initiator	Time	Yield %
Pyridine	3 hrs.	72
2, 4, 6 Collidine	24 hrs.	68
Quinoline	3 hrs.	75
Triethylamine	3 hrs.	52
HMPT	3 hrs.	65
Triethylamine	3 hrs.	70

(contd.)

TABLE 7 (contd.)

Initiator	Time	Yield %
Lithium tertiary Butoxide a.	3 hrs.	80
SbCl <sub>5</sub> b	1 week	58
Ti Cl <sub>4</sub> b	1 month	4
AlCl <sub>3</sub> b	3 hrs.	67
AlBr <sub>3</sub> b	3 hrs.	71
CsF	3 hrs.	63
CsCl	3 hrs.	60
CF <sub>3</sub> SO <sub>3</sub> H b	1 week	40
H <sub>2</sub> SO <sub>4</sub> b	1 week	31

a. 0.3 mole percent. b. Reaction Temperature -10°C  
initiator concentration. c. 1 mole %

#### A. Polymerization in the Presence of Anions

Tertiary amines, metal alkoxides, alkali metal chlorides or fluorides, and phosphonium chlorides were effective initiators for the polymerization of BDCA. All of these polymerizations were rapid at -30°C but some initiators were more efficient and produced more rapid reactions. All of the anionic polymerizations were gel forming if initiation was carried out above 40°C. Cryotachensic polymerizations took place, in a manner that visually closely resembled cryotachensic chloral polymerizations, as soon as the temperature of the reaction fell below the



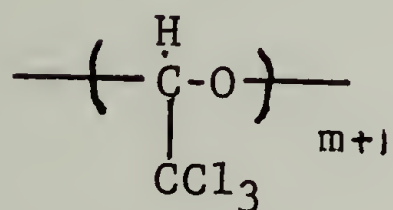
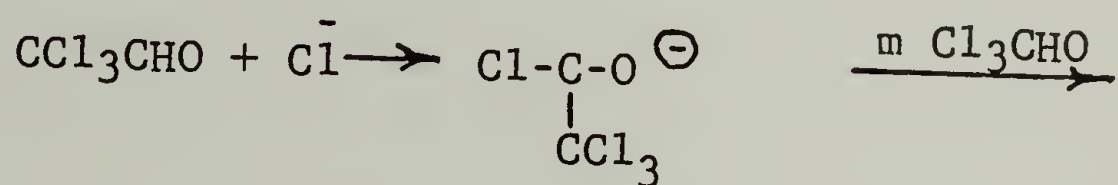
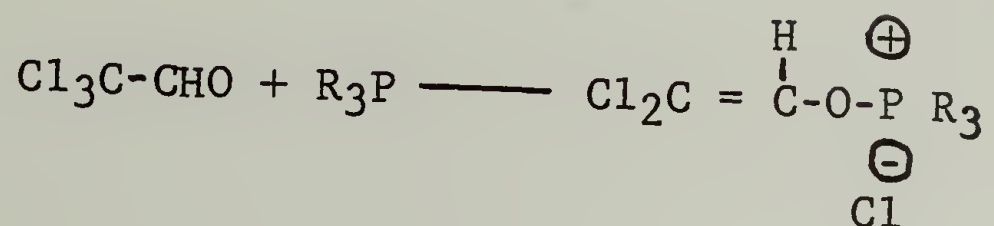
threshold temperature. A self-supporting gel appeared after five minutes, hardened, and became cloudy during the hour. Most of the reactions of  $\text{Cl}_2\text{CBrCHO}$  with anions appeared to be completed within one hour.

The yield of polymer, after extraction with acetone or dichloromethane, were about 70 percent. Some unstable polymer fractions were degraded by the extraction. The yields before extraction were higher than the values given in the table. The polymer obtained with triethylamine, as the initiator, were fairly unstable and the yield of crude polymer not extracted, was 20 percent higher (about 72%) before extraction.

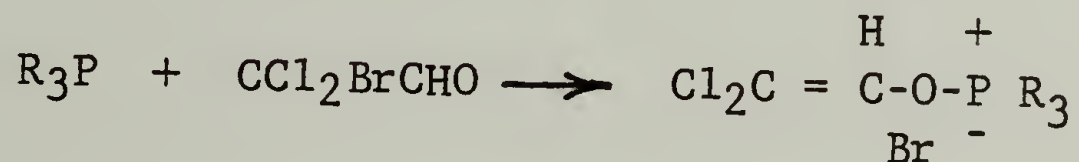
All nucleophiles that polymerized chloral also polymerized BDCA with two important exceptions. Tri-alkyl phosphines failed to polymerize  $\text{Cl}_2\text{CBrCHO}$  and bromide or iodide salts were not effective initiators. A series of experiments were devised to explain these results.

The identity of the true species present in the reaction of trialkyl phosphines with  $\text{Cl}_2\text{CBrCHO}$  was found to be essential. In the case of chloral a phosphonium chloride is formed when a trialkyl phosphine was reacted with the

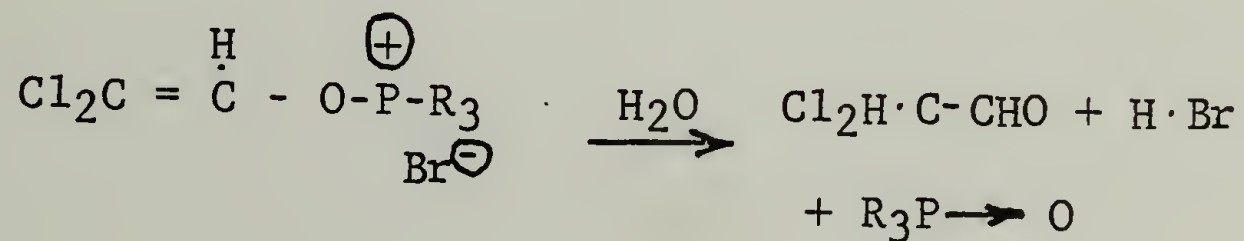
aldehyde and the chloride ion is the actual initiating nucleophile for the polymerization of chloral.



It was found that at 25°C triphenylphosphine reacted with  $\text{Cl}_2\text{CBrCHO}$  to form a phosphonium bromide.

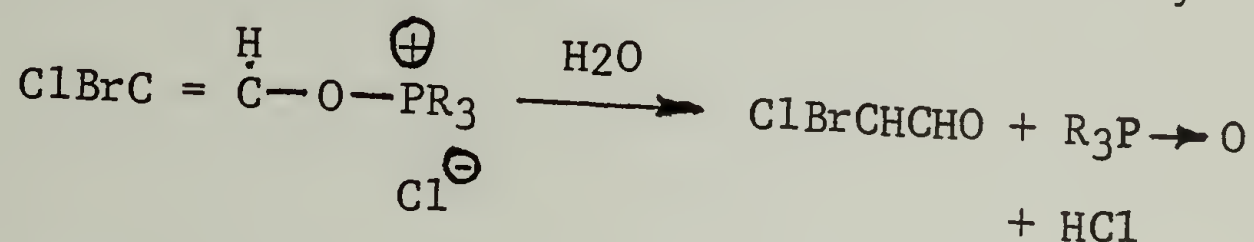


The identity of this salt was established by the analysis of its hydrolysis products.



Dichloroacetaldehyde was isolated as the sole aldehyde

product from this hydrolysis and bromochloroacetaldehyde was not observed. This product would have arisen if the phosphonium chloride had been formed preferentially.

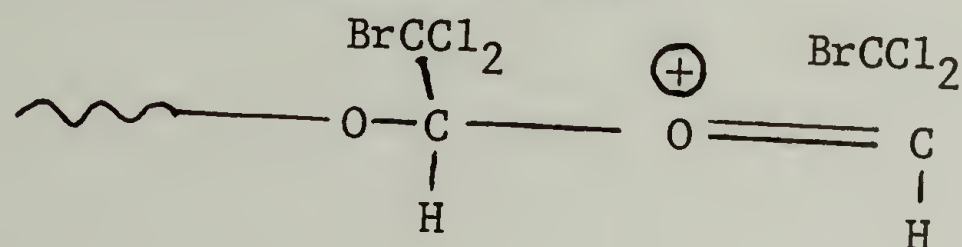


The  $\text{Ph}_3\text{P}/\text{Cl}_2\text{CBrCHO}$  adduct was isolated and purified. It failed to polymerize  $\text{Cl}_2\text{CBrCHO}$  but did polymerize chloral. The chloride salt, the chloral-triphenylphosphine 1.1 adduct did polymerize  $\text{Cl}_2\text{CBrCHO}$  and chloral. Furthermore, cesium bromide polymerized chloral but did not polymerize BDCA. Bromide ion appeared to be ineffective as an initiator for BDCA. Cesium iodide also failed to polymerize  $\text{Cl}_2\text{CBrCHO}$  so it was consequently concluded chloride and fluoride ions were effective initiators while bromide and iodide ions were not effective initiators for BDCA at an initiation of  $\text{Cl}_2\text{CBrCHO}$  at temperature of  $30^\circ\text{C}$ . When the initiation of BDCA was carried out at  $80^\circ\text{C}$  however a polymer was formed. An analysis of the reaction of triphenylphosphine with  $\text{Cl}_2\text{CBrCHO}$  at  $80^\circ\text{C}$  revealed that both dichloroacetaldehyde and bromochloroacetaldehyde were formed from the hydrolysis of the phosphonium salts.





of  $\text{H}_2\text{SO}_4$  to yield a white powder.<sup>(94)</sup> The polymerization of BDCA in the presence of  $\text{H}_2\text{SO}_4$  also yielded a white powder, but the yield was higher. Both chloral and BDCA polymerizations with  $\text{H}_2\text{SO}_4$  required induction periods before any polymer, insoluble in the monomers, was obtained. The induction period for the polymerization of BDCA was shorter than the induction period for the polymerization of chloral. The higher yield and shorter induction period may be due to the polarizability of the bromine in the CDCA. The polarizable electron cloud may stabilize the positive oxonium ion in the transition state.



Lewis acids, such as  $\text{SbCl}_5$  and  $\text{AlCl}_3$  were more effective than the protic acids as initiators for the polymerization of BDCA. In fact,  $\text{AlCl}_3$  polymerized BDCA rapidly to form a gel at a rate that was comparable to polymerization of BDCA in the presence of chloride ion. It is possible that the polymerizations in the presence of  $\text{SbCl}_5$  or  $\text{AlCl}_3$  were actually anionic.  $\text{SbCl}_5$  can exist in the form of  $\text{SbCl}_4^{\oplus}$  <sup>(149)</sup>  $\text{SbCl}_6^-$ , and initiation by chloride ion might be

possible. The yields of polybromodichloroacetaldehyde in the presence of  $\text{SbCl}_5$  or  $\text{AlCl}_3$  were almost as high as the yields in most anionic polymerizations of this monomer. Higher yields of chloral polymerizations were also observed in the presence of  $\text{SbCl}_5$  or  $\text{AlCl}_3$ .<sup>(94)</sup>

### C. Generation Observations

Several general observations were made with contrast the polymerizations of BDCA in the presence of nucleophiles as compared with the polymerizations in the presence of acids. Firstly the anionic polymerizations were gel forming, yielding coherent pieces of polymer, while the cationic polymerizations with one exception, were precipitation polymerizations. Secondly, the cationic polymerizations always had an induction period. Thirdly the yields were much higher in the anionic polymerizations.

### 2. Polymerization of CDBA

CDBA, freshly purified, polymerized in the presence of nucleophiles and in the presence of selected acids. The initiators, reaction conditions and yields are given in Table 8.

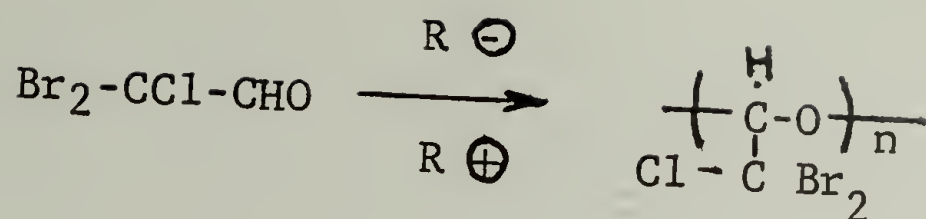


TABLE 8

BULK POLYMERIZATION OF CDBA AT  $-45^{\circ}\text{C}$   
Initiator Concentration 2 Mole %

Initiator	Reaction Time	Yield %
Pyridine	72 hrs.	52
Quinoline	72 hrs.	47
Li tert Butoxide	72 hrs.	30
SbCl	1 week	24
H <sub>2</sub> SO <sub>4</sub> a.	1 month	3
H <sub>2</sub> SO <sub>4</sub> b.	1 week	4
CF <sub>3</sub> SO <sub>3</sub> H a.	1 month	3
Cs Cl	72 hrs.	44
Cs F	72 hrs.	49
AlCl <sub>3</sub> / No <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	72 hrs.	38
(C <sub>2</sub> H <sub>5</sub> ) N <sup>+</sup> Cl <sup>-</sup>	72 hrs.	39
Ph P <sup>+</sup> -O-C = CCl <sub>2</sub>	72 hrs.	35
Cl <sub>-</sub>		

a. Polymerization temperature  $-20^{\circ}\text{C}$   
b. Polymerization temperature  $-78^{\circ}\text{C}$

a. Polymerization in the Presence of Nucleophiles

Tertiary amines, metal alkoxides, alkali metal chlorides or fluorides and phosphonium chlorides were effective initiators for the polymerization of CDBA. All of these polymerizations were completely or nearly complete after three hours at  $-45^{\circ}\text{C}$  but longer reaction times were

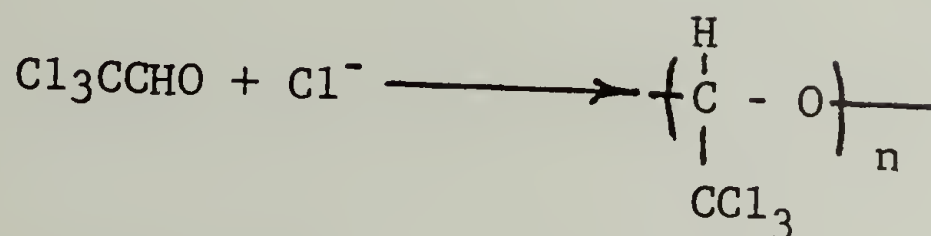
used to maximize conversions. All polymerizations were initiated above the polymerization threshold temperature. Gels were formed during these polymerizations when the polymerizations were maintained in the quiescent state at  $-45^{\circ}\text{C}$ . These cryotachensic polymerizations resembled closely the corresponding polymerizations of chloral and of BDCA. The yields of polymer, after extraction with acetone or dichloromethane were about 50%. Unstable polymer fractions were degraded by the extraction and the yields before extraction were higher than the values given in the table by about 10-15 percent.

The polymerization of CDBA in the presence of nucleophiles closely resembled the polymerization of BDCA. Most of the nucleophiles that polymerized chloral also polymerized CDBA and BDCA except the tri-alkyl phosphine and bromide or iodide salts. Their salts were halide.

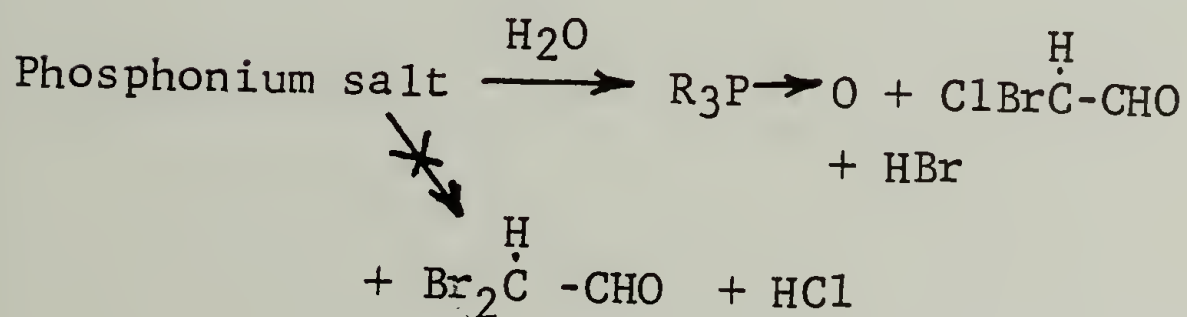
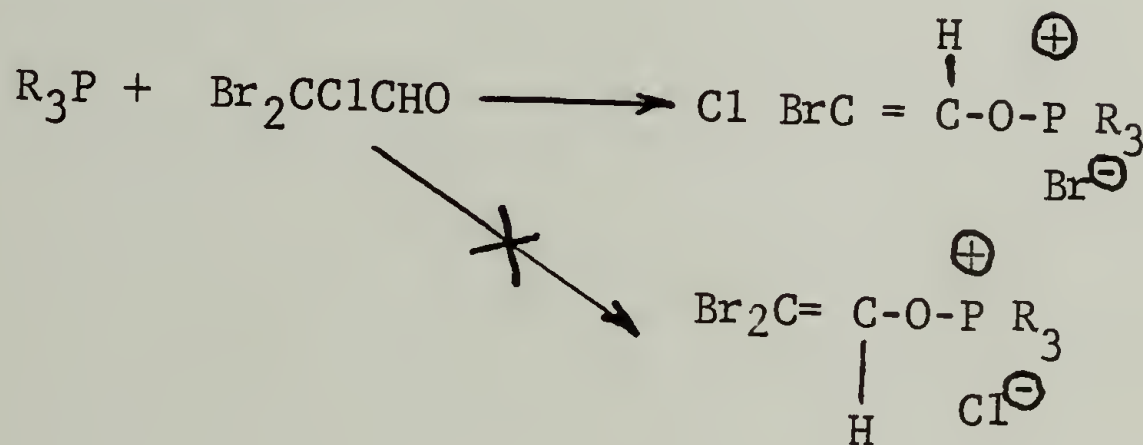
It was necessary to determine the identity of the true species present in the reaction of triphenylphosphine with  $\text{Br}_2\text{CCl CHO}$ . In the case of chloral a phosphonium chloride is formed when a triphenylphosphine was added to chloral. The chloride ion is then the actual initiator in the



polymerization of chloral.



Triphenylphosphine reacted with  $\text{Br}_2\text{CClCHO}$  to form a phosphonium bromide.



A 1:1 crystalline reaction product of triphenylphosphine and CDPA was prepared and the resulting phosphonium salt was hydrolyzed to give CBA but no dibromoacetaldehyde. The reaction sequence above shows that if a chloride salt

were present, dibromoacetaldehyde would have been present in the hydrolysis products, but it was not detected. The bromochloroacetaldehyde has been reported<sup>(150)</sup> and the physical constants observed in this work were similar to those reported before. This analysis indicated that triphenylphosphine reacted with CDBA and bromide ion was preferentially lost, and it is proposed that bromide ion is not an effective initiator for CDBA. Tri-n-butyl phosphine also failed to polymerize CDBA under the conditions used.

b. Polymerization of CDBA in the Presence of Acids

The polymerization of CDBA in the presence of nucleophiles closely resembled in most cases the anionic polymerizations of BDCA and  $\text{Cl}_3\text{C CHO}$  except that lower temperatures were required for the polymerization of CDBA, but CDBA under these conditions was somewhat less reactive than  $\text{CCl}_3\text{CHO}$  and BDCA.

The yields and the reaction rates for the polymerization of CDBA in the presence of acids were also markedly lower than for chloral and BDCA. After one month  $\text{H}_2\text{SO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  polymerized CDBA in yields of 1% and 3% respectively. These values were much lower than the yields

observed for the polymerizations of BDCA in the presence of these acids. The yields of polychlorodibromoacetaldehyde were the same at  $-20^{\circ}\text{C}$  or at  $-78^{\circ}\text{C}$  when CDBA was polymerized with  $\text{CF}_3\text{SO}_3\text{H}$ .

CDBA also polymerized in the presence of antimony pentachloride in a yield of 24%. The rate at which polymer formed in this reaction was much lower than the rate at which polybromodichloroacetaldehyde or polychloral appeared under similar conditions.

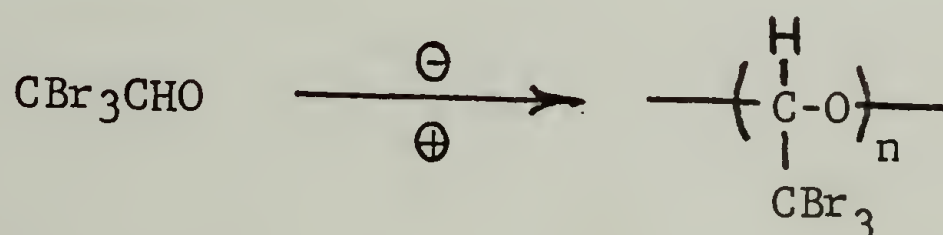
Steric effects may be very important in the polymerizations of BDCA and CDBA in the presence of acids. These steric effects may be less important in the anionic polymerizations of these two monomers since the yields and reaction times under anionic conditions were nearly equal for BDCA and CDBA.

CDBA polymerizations as other haloaldehyde polymerizations were particularly sensitive to the presence of impurities and to the methods of initiation. All the successful polymerizations were carried out in vacuum sealed tubes with freshly purified monomer. Usually better yields were obtained when the initiators were added as solutions in the

toluene. Particularly in the cases of the tertiary amines better yields were obtained when they were added as 1 molar solutions in dry toluene.

### 3. Polymerization of Bromal

Bromal, when purified according to the procedure described above, polymerized in the presence of nucleophiles and in the presence of trifluoromethane sulfonic acid at low temperatures.



The initiators, reaction conditions and yields are given in Table 9.

TABLE 9

Polymerization of  $\text{Br}_3\text{CCHO}$  Solvent:  
Toluene (20%) at  $-78^\circ\text{C}$  for 72 hours

Initiator (2.5 mole %)	Time	Yield %
Pyridine	72 hrs.	46
Quinoline	72 hrs.	39
$\text{Et}_3\text{N}$	72 hrs.	48
Li tert Butoxide <sup>a</sup>	72 hrs.	16
$\text{CH}_3\text{SO}_3\text{H}$	1 month <sup>b</sup>	3

a. 0.3 mole %

b. Reaction time 1 month



a. Polymerization in the Presence of Nucleophiles

Tertiary amines and metal alkoxides polymerized bromal rapidly at  $-60^{\circ}\text{C}$  or  $-78^{\circ}\text{C}$ . Quinoline, triethylamine and pyridine were added as one molar solutions in toluene at room temperature to bromal in polymerization tubes (above the threshold polymerization temperature) and the mixture was cooled. Self-supporting gels were formed after one hour at  $-78^{\circ}\text{C}$ . The yields were lower for bromal polymerizations than for the homopolymerizations of the other three monomers, chloral, BDCA, and CDBA.

Several important considerations were important for the successful polymerization of bromal.

1. The monomer purity required was much greater than the monomer purity necessary for chloral polymerizations.

Bromal, in order to be satisfactory for polymerization, should contain not more than 0.1% total impurities. Repeated distillation of bromal from phosphorous pentoxide did not remove the impurities. Several impurities persisted, according to analyses by gas chromatography, after it was freshly distilled from phosphorous pentoxide. If bromal was heated over antimony trifluoride at  $100^{\circ}\text{C}$  and

then distilled from phosphorous pentoxide the small peaks in the G.C. disappeared. Phosphorous pentoxide was able to remove water, but was not able to remove two other impurities. Bromal purified with antimony trifluoride was virtually colorless which demonstrated that antimony fluoride was necessary for the production of polymerization grade monomer.

2. The second important requirement for the bromal polymerization was the necessity of a diluent with a very low melting point. Pure bromal crystallizes at temperatures well above the threshold polymerization temperature and no polymerization took place if a liquid state was not maintained. Also, bromal recrystallized from methyl cyclohexane and other solvents at a temperature that was well above the threshold polymerization temperature. Toluene however prevents bromal crystallization. Pure bromal would not solidify and would not crystallize out if a sufficient amount of toluene was present. In the absence of toluene no polymerization took place.

3. The third requirement for bromal polymerization was

the method of initiation. If the initiator was added as a one molar solution in toluene then local high concentrations of initiator were avoided and mixing of the initiator with the monomer was more complete. When pyridine was used at high concentration a red side product was produced which probably inhibited the polymerization and only a low yield of polymer was isolated.

4. The fourth important requirement was the temperature program used for the polymerizations. Yields of polymer were higher when the polymerization tubes were first cooled to  $-60^{\circ}\text{C}$  for a few minutes and then cooled to  $-78^{\circ}\text{C}$ . If the polymerization was conducted at  $-78^{\circ}\text{C}$  part of the bromal crystallized out immediately but at  $-60^{\circ}\text{C}$  this was not observed. A self-supporting gel formed initially and if the tube was then placed in the  $-78^{\circ}\text{C}$  bath, the monomer crystallization did not take place and all of the monomer was available for polymerization.

A special remark must be made about the polymerization of bromal with lithium tertiary butoxide. If lithium tertiary butoxide was added to bromal at  $25^{\circ}\text{C}$  and the

initiated monomer was cooled to  $-78^{\circ}\text{C}$  no polymer formed. A small quantity of white solid precipitated and the white solid was isolated and found water soluble. A side reaction; the formation of lithium bromide, took place at  $25^{\circ}\text{C}$ . If, however, the lithium tertiary butoxide was added to the bromal at a low temperature, well below  $0^{\circ}\text{C}$ , then initiation took place and polybromal could be isolated.

Several initiators which polymerized chloral did not polymerize BDCA or CDBA and also did not polymerize bromal: triphenyl phosphine, tri-n-butyl phosphine, cesium bromide, and cesium iodide.

b. Polymerization of Bromal with Acids

Several protic acids and several Lewis acids were employed as possible initiators for the polymerization of Bromal. Only one acid, trifluoromethane sulfonic acid, produced polymer. The yield was only about three percent after one month. Antimony pentachloride, one of the most efficient cationic initiators for the polymerization of  $\text{CCl}_3\text{CHO}$ , CDBA and BDCA was not an effective initiator for bromal at  $-78^{\circ}\text{C}$ .



### Summary

The monomers of  $\text{Cl}_2\text{CBrCHO}$ ,  $\text{Br}_2\text{CClCHO}$  and  $\text{Br}_3\text{CCHO}$  each homopolymerized in the presence of nucleophiles to high conversions, at rates and conversions which were very similar for all three aldehydes. The rates of polymerization and the conversions decreased in the order  $\text{Cl}_2\text{CBrCHO}$   $\text{Br}_2\text{CClCHO}$   $\text{Br}_3\text{CCHO}$  which was interpreted on the basis of an increase in the bulkiness of the side group.

#### 4. Polymerization Rate Measurements for CDBA, BDCA, and Bromal by PMR Spectroscopy

The rate of homopolymerization of the three monomers BDCA, CDBA, and bromal with pyridine and with  $\text{CF}_3\text{SO}_3\text{H}$  were measured by measuring the decrease in the aldehyde proton intensity of a polymerizing solution in vacuum sealed NMR tubes. The monomers and initiators were mixed in the tubes above the polymerization threshold temperatures and then the tubes were kept at the prescribed bath temperature and then removed for measurement. It was shown that no polymerization or depolymerization took place during measurement.

The polymerization of aldehydes below the threshold temperature is effected by the efficiency of heat removal.

In the first set of experiments an attempt was made to remove the heat from each polymerization at the same rate. A bath temperature for each monomer was set so that a constant difference between this temperature and the threshold temperature was maintained. The homopolymerization rates of BDCA, CDBA, and bromal with 2.5 mole percent pyridine at a bath temperature of approximately  $T_c \text{ bulk} - T_{\text{reaction}} = 40^\circ\text{C}$  were determined. The percent conversions as a function of time are shown in Appendix 3.

The final equilibrium conversions decreased in the order BDCA, CDBA, bromal. The data also indicate that the rates of polymerization followed this order but that they were very similar. All the polymerizations were essentially complete in one hour.

A second set of measurements of the polymerization rates were made at a bath temperature of  $-78^\circ\text{C}$ . The plot of percent conversion against time is shown in Appendix 3. The data show that the polymerization of  $\text{Cl}_2\text{C BrCHO}$  was very rapid at  $-78^\circ\text{C}$ .

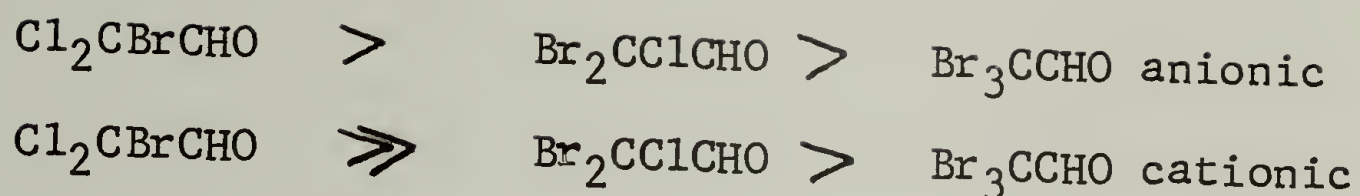
The temperature of polymerization of these monomers with pyridine, had little effect on the final conversion but

a profound influence on the rate if the temperature was well below the ceiling temperature.

The rates of homopolymerization of BDCA and CDBA and bromal in the presence of trifluoromethane sulfonic acid are shown in Appendix 3 where percent conversion is plotted against reaction time. BDCA in the presence of this acid polymerized after an induction period of several hours. The polymerization was complete after 72 hours and the conversion was 40%. Chlorodibromoacetaldehyde in the presence of  $\text{CF}_3\text{SO}_3\text{H}$  showed very little change in the intensity of the aldehyde carbonyl proton in the NMR spectra during a one month period. The low yield of polymer observed in the polymerization reaction of CDBA with  $\text{CF}_3\text{SO}_3\text{H}$  was due to the failure of this monomer to form a chain molecule and was not due to a side reaction. A low yield of polymer was also obtained from bromal.

The data from the NMR experiments agreed closely with the previous data on polymerization rates and conversions for these three monomers. The order of reactivity of these monomers were:





The following explanation is proposed. This order of reactivity corresponds to the order of increasing side group size. The steric hinderance was the greatest in bromal and it was the least reactive. The influence of steric hinderance in the cationic polymerizations was great while the influence of steric hinderance on rates and conversions in the anionic polymerizations was not as important.

## 5. Polymerization Threshold Temperatures

An experiment was designed to determine the polymerization threshold and ceiling temperature of polymerizations for BDCA, CDBA, and bromal. The polymers were insoluble in the monomers, and the appearance of a cloudiness at a certain temperature in a solution of chloral polymerization has been interpreted as the onset of polymerization.<sup>(69)</sup> The visual observation of the cloud temperatures at different monomer concentrations has been used to determine ceiling temperatures.<sup>(69)</sup> In this study an instrumental method was used for this determination of the cloud temperatures of



these monomers at various concentrations. A light source and a sensitive detector were used to measure the decrease in intensity of light transmitted through a sealed tube containing the initiated monomer.

A photograph in the apparatus is in Appendix 6.

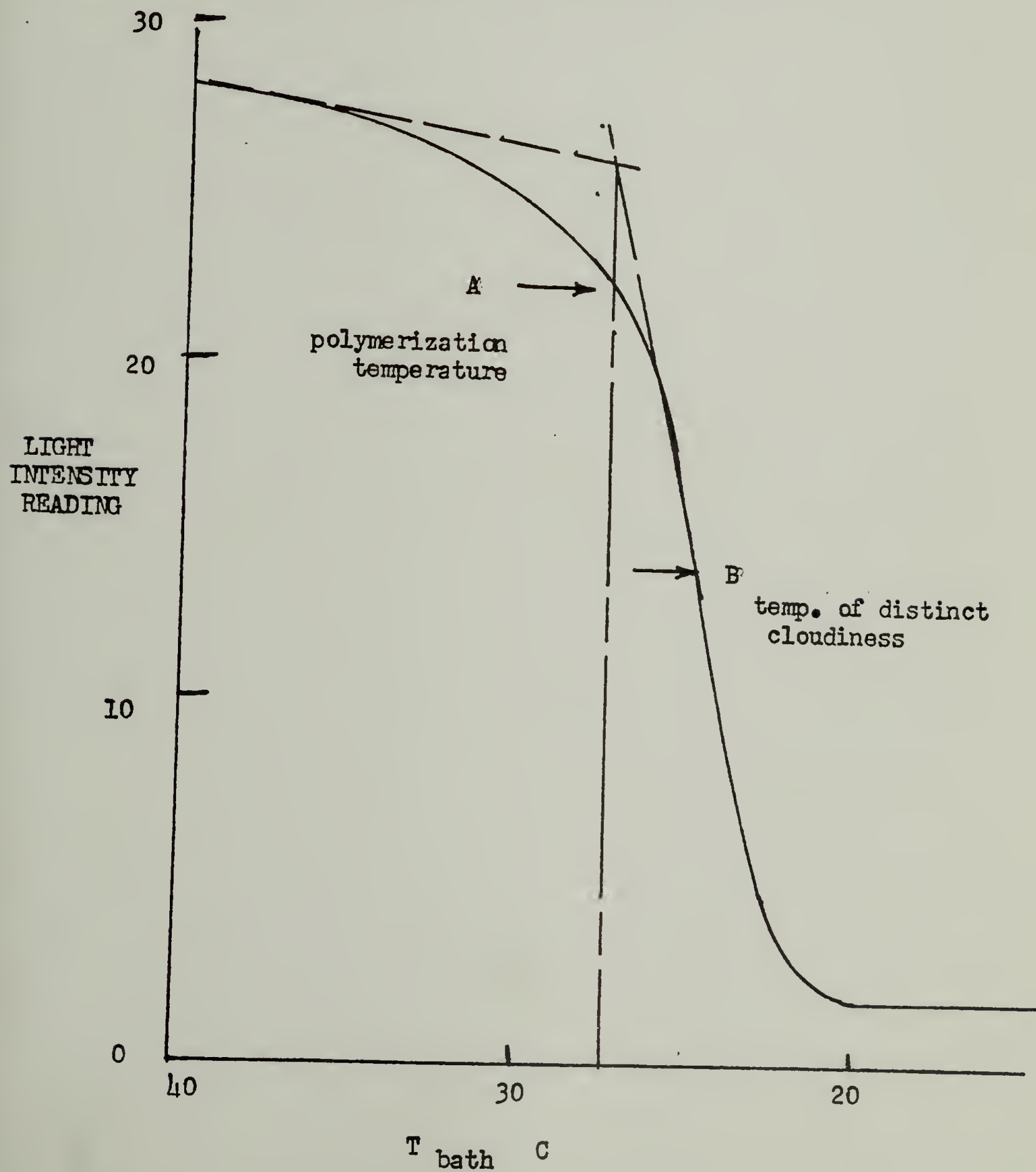
A plot of the intensity as a function of temperature for CDBA in toluene with pyridine is shown below and is typical of the data taken for all of the monomers.

(See Figure 1, p. 220) The data on the figure show a rapid decrease in light intensity after a slow decrease. The point of maximum slope is the point (B) where the unaided eye detected the first cloudiness. The threshold temperature was taken to be at point (A) where the slope changes most rapidly. Point B is the visual cloud point and at this point some polymer precipitated and the process was no longer an equilibrium polymerization. Therefore Point B was not a true threshold temperature and Point A was chosen instead.

The measurements were made at several monomer concentrations in toluene. Pyridine was used as the initiator in all cases. The ceiling temperature for each monomer was

FIGURE 1

THRESHOLD POLYMERIZATION DATA FOR BDCA IN TOLUENE  
INITIATOR: PYRIDINE MONOMER CONCENTRATION 8.33 MOLAR  
TRANSMITTED LIGHT INTENSITY vs. BATH TEMPERATURE



obtained by extrapolating the experimental points on a plot of  $1/T_{\text{POLYM.}}$  vs.  $\log [M]$ . The ceiling temperatures for one molar solutions in toluene are given in Table 10.

TABLE 10

CEILING TEMPERATURES OF PREHALOALDEHYDES 1M SOLUTION  
IN TOLUENE. INITIATOR: PYRIDINE

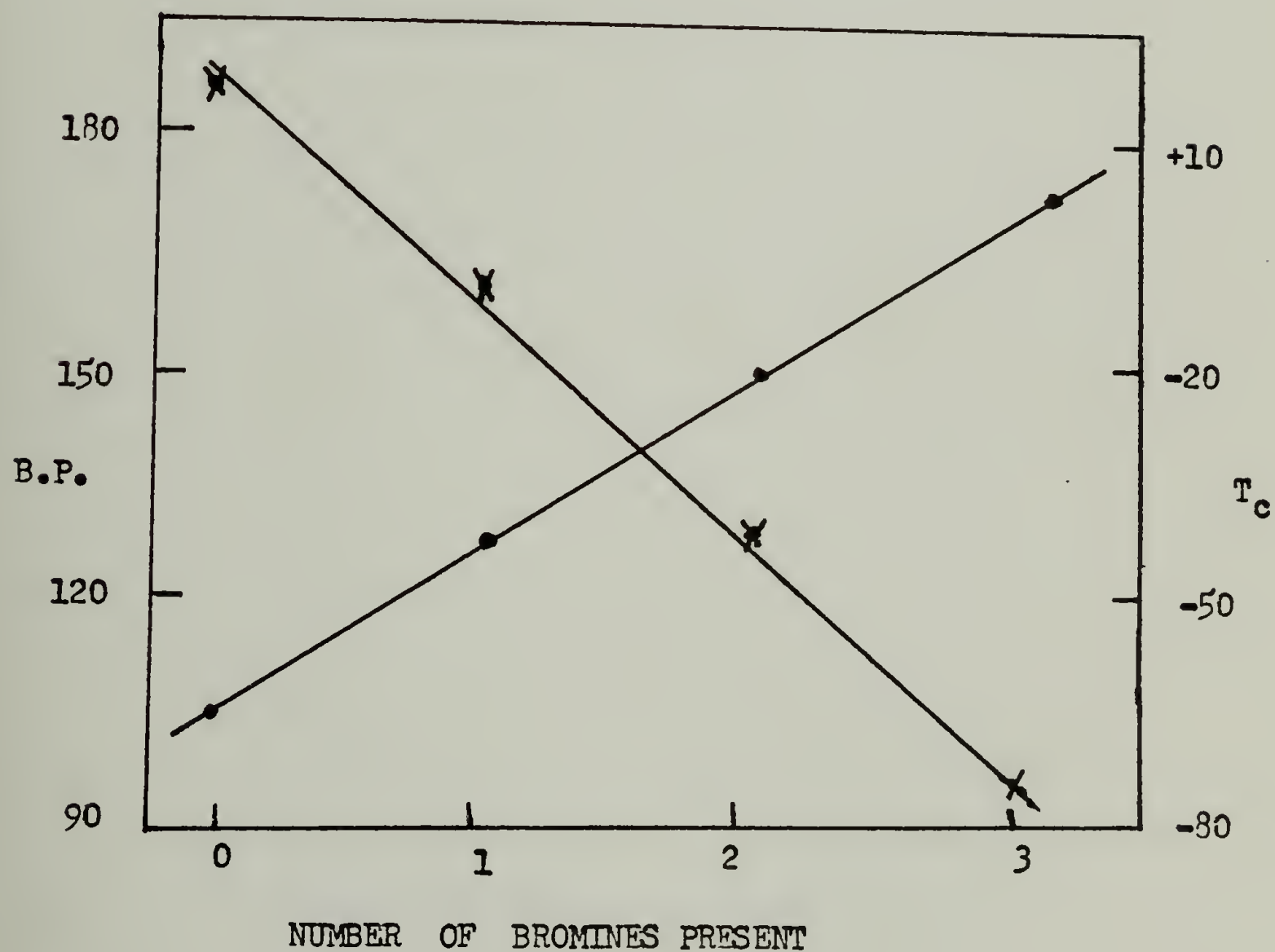
Chloral	+18°C
BDCA	-11°C
CDBA	-45°C
Bromal	-75°C

The ceiling or threshold polymerization temperatures decreased as the side group size increased. Increased steric hinderance would be expected to make the polymerization less thermodynamically favorable and would lower  $T_c$ . The polymerization decreased linearly with the number of bromine atoms in the aldehydes. The monomer boiling points of these compounds increased linearly. A plot of  $T_c$  and boiling point for each monomer and for chloral is shown in Figure 2 on page 222.

FIGURE 2

X: CEILING TEMPERATURES vs. NO. OF BROMINES PRESENT IN  
CHLORAL, DCBA, DBCA and BROMAL (1 M in TOLUENE)

: BOILING POINTS OF ALDEHYDES (DEGREES CELCIUS)





E. Copolymerization of Fully Halogenated Bromoacetaldehydes.

1. Copolymerization with Chloral

CDBA and BDCA and bromal each copolymerized with chloral in the presence of anions and certain acids. The reactants, reaction conditions, and yields of copolymers are given in Table 11. (See page 224)

Infrared spectra, vacuum degradation data and elemental analysis indicated that  $\text{Cl}_2\text{CBrCHO}$  and  $\text{Br}_2\text{CClCHO}$  copolymerized under anionic or cationic conditions with chloral. High amounts of BDCA or CDBA were present in the copolymer at high polymerization feed ratios. Bromal in contrast was very reluctant to copolymerize with chloral under all reaction conditions, and may be interpreted by the relative inability of bromal to fit into the polychloral chain because of the size of the tribromomethyl group.

The data in Table 11 also indicate that the reactivities of CDBA and BDCA in copolymerizations with chloral were higher under cationic conditions than under anionic conditions. Under anionic conditions chloral is known to polymerize rapidly at temperatures which were below the

TABLE 11

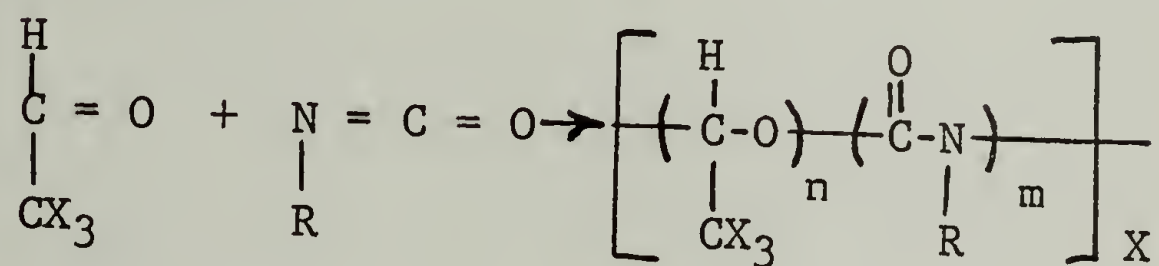
Copolymerizations of Chloral with BDCA, CDBA, and Bromal  
Initiator Concentration 2 Mole %

Comonomer	% Chloral in Feed	Polymerization temp. °C	Polymerization time, hrs.	Initiator	Conversion %	Comonomers in Product %
Cl <sub>2</sub> CBrCHO	75.0	-30	3	Pyridine	68	59
	50.0				71	36
	25.0				70	23
	75.0	-45	15	CF <sub>3</sub> CO <sub>3</sub> H	46	62
	50.0				43	49
	25.0				36	35
Br <sub>2</sub> CClCHO	75.0	-45	3	Pyridine	57	28
					63	10
					50	3
Br <sub>3</sub> CCHO	50.0	-10	316	CF <sub>3</sub> SO <sub>3</sub> H	43.9	40
	25.0				40.6	27
	50.0				35.6	11
	25.0					
	75.0		72	Pyridine	41	0
	50.0				30	0
	25.0	-78	316	CF <sub>3</sub> SO <sub>3</sub> H	18	0
	75.0				17	0
	50.0				12	0
	25.0				8	0

polymerization temperature of BDCA or CDBA. CDBA was very reluctant to homopolymerize under cationic conditions, but it copolymerized readily with chloral.

## 2. Copolymerization with Isocyanates

BDCA, CDBA, and bromal copolymerized with Ahyl and alkyl isocyanates.



The monomer feed ratios, reactions conditions, and yields are described in Table 12 (page 226).

Data in Table 12 indicate that each of the three aldehydes differed in their reactivity with phenyl isocyanate. Bromal was less reactive than BDCA toward phenyl isocyanate. Consequently a greater amount of phenyl isocyanate copolymerized with bromal than with BDCA at 50 percent concentrations in the feed. CDBA was intermediate in reactivity. 38% isocyanate in CDBA phenyl isocyanate copolymer was less than 50% in bromal phenyl isocyanate copolymers, but more than 32% in BDCA, phenyl isocyanate copolymers.

TABLE 12

Copolymerization of Prehaloacetaldehydes with Isocyanates  
 Initiator: Pyridine (2.5 mole %) Reaction Temp.  $-78^{\circ}\text{C}$ .

Monomer	Comonomer	$[M_1]$ ( $M_2$ )	% Conversion	% Isocyanate in Product <sup>b</sup>
BDCA				
	50		84.0	32
PhNCO	20		70.6	16
	10		73.7	13
	5		66.1	7
BuNCO	50		38.2	7
CDBA				
	50		91	38
PhNCO	20		46.4	27
	10		54	13
	5		52	8
BuNCO	50		22.1	7
Bromal				
BuNCO	55, 50		74	50, 46
	20		61.1	13.1
	10		50.4	11.0
	5		34.0	6
CH <sub>3</sub> PhNCO	50		42.0	16
BuNCO	50		48.4	7, 9

a. Initiator Concentration 2.0 mole %.

b. Determined by elemental analysis for nitrogen.



At high isocyanate concentrations bromal formed a nearly 1:1 copolymer with phenyl isocyanate under anionic conditions according to analyses for nitrogen and bromine. Only this copolymer (with a molecular weight of 7000 according to vapor phase osmometry) was soluble in dichloromethane. The copolymers of BDCA and CDBA with phenyl isocyanate were insoluble in  $\text{CH}_2\text{Cl}_2$  but the amount of isocyanate in the copolymer was always less than 50%.

Phenyl isocyanate was much more reactive in copolymerizations with BDCA, CDBA and bromal than was n-butyl isocyanate and p-methylphenyl isocyanate were. For example when 1:1 mixture of n-butyl isocyanate and bromal were polymerized the product isolated contained only about 7% isocyanate according to nitrogen analysis. The p-methylphenyl isocyanate was less reactive than phenyl isocyanate but more reactive than n-butyl isocyanate in copolymerizations with bromal, BDCA and CDBA.

The yields recorded for the copolymerizations of CDBA, BDCA, and bromal were slightly higher than the yields for the homopolymerizations of the aldehydes. The copolymers were more thermally stable than the homopolymers and the

extraction with acetone did not cause any appreciable degradation of the copolymers. In contrast the extraction degraded some unstable homopolymer fractions.

Many of these bromoacetaldehyde-isocyanate copolymers could be separated into two fractions when the polymerization mixture was treated with  $\text{CH}_2\text{Cl}_2$ . One fraction when removed from the polymerization tube was insoluble in  $\text{CH}_2\text{Cl}_2$  and the other fraction was soluble. The copolymers, while still swollen with monomer could be separated into two fractions with dichloromethane. The soluble fraction could be precipitated with n-hexane. However, after the soluble fraction was collected and dried it could not be redissolved in  $\text{CH}_2\text{Cl}_2$ .

#### F. Homopolymer Characterization

##### Infrared Spectra of Homopolymer

The empirical formulas of the products isolated were established as being identical to the empirical formulas of the respective monomers by elemental analyses. The infrared spectra of those homopolymers in the range of  $4000\text{-}250\text{ cm}^{-1}$  were very similar to published infrared spectra of polychloral. In a recent study<sup>(73)</sup> a detailed

analysis of the infrared spectra of polychloral was published and assignments of absorptions to functional groups in the polymer were made.<sup>(73)</sup> The assignments are summarized in Table 13.

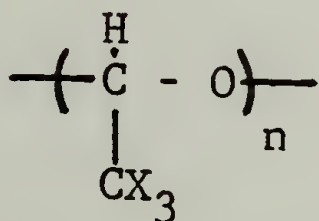
TABLE 13

INFRARED SPECTRUM OF POLYCHLORAL<sup>(73)</sup>

Wave number $\text{cm}^{-1}$	Intensity	Motion
3500	vs	OH stretching
3360	w	OH stretching
2945	m	C-H stretching
2910	w	C-H stretching
1386	w	combination 803+582
1360	m	C-H bending
1325	s	C-H bending
1122	vs	C-O stretching
1085	vs	C-H stretching
1070	vs	C-O stretching
1028	m	C-H bending ?
975	vs	C-O stretching
842	vs	
830	vs	C-C and C-Cl
803	vs	Stretching
681	s	C-Cl stretching
675	s	C-Cl stretching
630	w, sh	skeletal non cryst.
582	s	C-Cl stretching

The infrared spectra of the polymers of BDCA, CDBA and bromal are shown in Appendix 2. The spectra are also superimposed on one page to show the great similarity of

the three spectra and their similarity to the spectrum of polychloral. The carbon-hydrogen stretching in all samples was observed near  $2940\text{ cm}^{-1}$ . The strong lines at  $1340\text{ cm}^{-1}$  and  $1325\text{ cm}^{-1}$  in polychloral were also present in the other three homopolymers. These two lines arose from C-H bending motions on each homopolymer. The absorptions in the region  $1200\text{-}900\text{ cm}^{-1}$  for the three spectra can be nearly superimposed on absorptions in a polychloral spectrum. These absorptions have been assigned to C-O stretching vibrations.<sup>(72)</sup> The similarity in the infrared spectra in the  $1200\text{-}900\text{ cm}^{-1}$  region indicates that all four homopolymers have carbon oxygen single bonds and they have the structure



and are substituted polyacetals. Differences between the spectra occur at longer wavelengths where the carbon-chlorine and carbon-bromine stretching modes would be expected.



### Evidence for a Helical Structure

Polychloral is isotactic or largely isotactic in every case studied. An helical structure was proposed for polychloral on the basis of a careful analysis of the infrared data summarized above in Table II. Polychloral and the three new homopolymers reported here are very similar in the carbon-hydrogen bending region and in the carbon oxygen single bond stretch region. The polymer chains present in polybromal, polychlorodibromoacetaldehyde, and polybromodichloroacetaldehyde, prepared with anionic initiation, are also probably helical and therefore isotactic. The infrared spectra of isotactic polyfluoral are very similar to our polymers. The spectra of atactic polyfluoral are very different than our polymers in the  $900\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  region.

The lines observed in the region  $1400\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  are listed in Table 13 for the homopolymers of chloral, BDCA, CDBA and bromal.

TABLE 14

INFRARED SPECTRA OF HOMOPOLYMERS OF CDBA, BDCA, BROMAL AND  
CHLORAL (KBr). ( $\pm 2 \text{ cm}^{-1}$ )

$\text{Cl}_3\text{CCHO}$	$\text{Cl}_2\text{CBrCHO}$	$\text{Br}_2\text{CClCHO}$	$\text{Br}_3\text{CCHO}$
1386	1375	1372	1382
1360	1350	1348	1355
1325	1311	1320	1322
1122	1109	1115	1142
1085	1068	1075	1-19
1070	1052	1040	985
975	949	943	

#### Infrared Spectra of Cationic Homopolymers

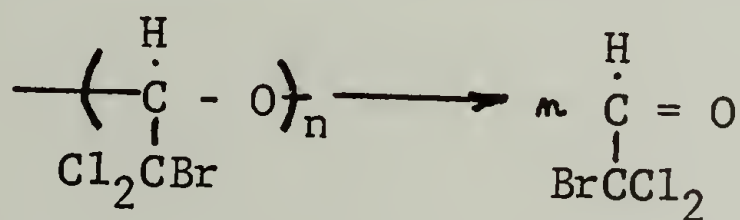
The homopolymers of  $\text{Cl}_2\text{CBrCHO}$ ,  $\text{Br}_2\text{CClCHO}$  and bromal prepared in the presence of acids displayed infrared spectra which were very similar to spectra described above.

Homopolymers of BDCA and CDBA obtained with  $\text{H}_2\text{SO}_4$  or  $\text{CF}_3\text{SO}_3\text{H}$  as initiators contain hydroxyl end groups. Two weak broad bands were observed at  $3350 \text{ cm}^{-1}$  and  $3500 \text{ cm}^{-1}$  which were probably due to hydroxyl end groups. If these samples were treated with  $\text{P Cl}_5$  in  $\text{CCl}_4$  then the two bands vanished. The spectra of the treated samples could then be superimposed on the rest of the homopolymer spectra.

## Vacuum Degradations

### Polybromodichloroacetaldehyde

When the polymer BDCA with pyridine as the initiator was heated in a sealed and evacuated tube, all of the solid polymer had degraded. The volatile products were trapped at one end of the evacuated tube which was cooled with liquid nitrogen. Analysis of the volatile materials by gas chromatography revealed that the polymer had degraded 98% to monomer, and by gas chromatography analysis shown in Appendix 1, that the volatile products consisted of 98% BDCA. There was 2% of char left behind in the heated end. This vacuum degradation added further support to the structural assignment for this polymer.



### Polychlorodibromoacetaldehyde

Polychlorodibromoacetaldehyde prepared with pyridine at  $-45^\circ\text{C}$  was degraded in a sealed evacuated tube. The volatile products produced were collected in a cold end which was cooled to liquid nitrogen. Analysis of these

volatile degradation products by gas chromatography revealed that they were 98% CDBA. This behavior added further support to the structural assignment for this polymer.



### Polybromal

Polybromal obtained with pyridine at  $-78^\circ\text{C}$  was thermally degraded in a sealed and evacuated tube without any char formation. The volatile products produced were analyzed by gas chromatography. The volatile product was 97% bromal by volume. This degradation data added support to the structural assignment of polybromal a substituted polyoxymethylene.

### Differential Thermal Analysis of Homopolymers

The thermal stabilities of each homopolymer were determined by differential thermal analysis. Different initiators produced polymers of differing thermal stabilities. These thermal stabilities were determined after the polymeric samples had been thoroughly extracted to remove traces of initiator which might catalyze the



degradation.

The polymers, initiators used in their synthesis, and their maximum degradation rate temperatures, are listed in Table 15. All of the degradation rate data were taken in the derivative mode so that the maxima were clearly available. (Table 15, p. 236)

Several observations can be made from the data in Table 15.

1. Homopolymers obtained in the presence of acid were more stable than homopolymers obtained in the presence of pyridine.
2. Homopolymers obtained when pyridine was the initiator had one maximum in the DTG curve. No char remained in the sample pan.
3. Homopolymers obtained under acid conditions usually had 2 or 3 maxima and a small amount of char remained in all cases in the sample pan.
4. The polymers which were treated with  $\text{PCl}_5$  were substantially more stable than the untreated anionic polymers. Treated polymers were similar in stabilities than homopolymers, prepared with cationic initiators.

TABLE 15

DTG MAXIMA  $\overset{\text{O}}{\text{C}}$  OF HOMOPOLYMERS OF CDBA, BDCA AND BROMAL  
Heating Rate 20°C/min. in Nitrogen

Monomer	Initiator	Max 1	Max 2	Max 3
BDCA	Pyridine	144	-	-
BDCA	H <sub>2</sub> SO <sub>4</sub> insol fcn			
BDCA	H <sub>2</sub> SO <sub>4</sub> sol fcn	153	199	240
BDCA	CF <sub>2</sub> SO <sub>3</sub> H			
BDCA	SbCl <sub>5</sub>	285	315	
BDCA	Pyridine PCl <sub>5</sub> treated		280	315
CDBA	Pyridine	120	-	-
CDBA	H <sub>2</sub> SO <sub>4</sub>		238	280
CDBA	CF <sub>3</sub> SO <sub>3</sub> H		249	
CDBA	SbCl <sub>5</sub>		-	300
CDBA	Pyridine PCl <sub>5</sub> treated		255	280
Bromal	Pyridine	146	-	-
Bromal	Pyridine PCl <sub>5</sub> treated		230	283

The single maximum in the DTG curve for the polymers obtained with pyridine was due to a quantitative degradation to monomer because of indicated unstable chain ends. The multiple maxima at high temperatures indicated the presence of chain ends of different and higher thermal stability. Breakage of the main chain probably took place at 280-300°C where the highest temperature maximum was observed.

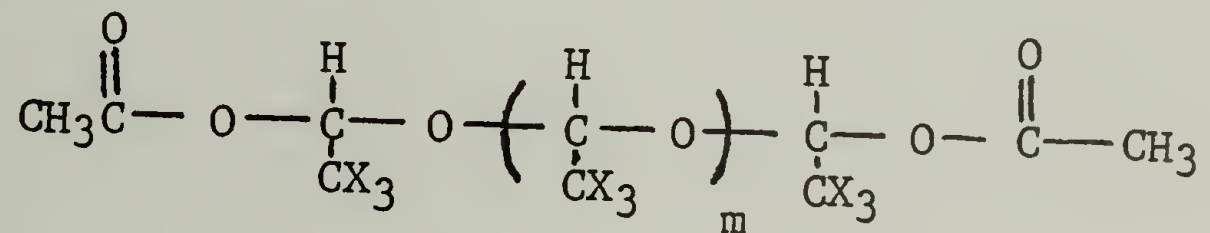
#### Analysis by Differential Scanning Calorimetry of BDCA, CDBA, and Bromal Polymers

Thermally stabilized homopolymers of BDCA, CDBA and bromal (stabilized by treatment with  $\text{PCl}_5$  in  $\text{CCl}_4$ ) were analyzed by DSC from -80°C to 300°C. Stabilized polychloral samples were also analyzed by DSC for comparison. No first order transitions and no second order thermodynamic transitions could be detected below the decomposition temperatures for these homopolymers. Polymer chains may be so rigid and so polar that the  $T_g$  and  $T_m$  are above the decomposition temperatures.

### Solubility in Organic Liquids

The homopolymers of BDCA, CDBA and bromal were tested for solubility in acetone,  $\text{CH}_2\text{Cl}_2$ , DMSO, Toluene, Hexane, HFIP, Trifluoroacetic acid, o-chlorophenol, and DMF and were found to be insoluble. Several oligomers of BDCA obtained by initiation of BDCA with  $\text{H}_2\text{SO}_4$  or  $\text{CF}_3\text{SO}_3\text{H}$  were isolated and were soluble in dichloromethane. These soluble fractions were 30% or less by weight of the total amount of polymer isolated.

These soluble fractions were end capped with acetylchloride or acetic anhydride and the number average molecular weights of these fractions were obtained by NMR spectroscopy. The acetyl protons and the backbone protons could be clearly seen and identified in the PMR spectrum (Appendix 2).



The integration of the protons indicated that the  $\text{DP}_n$  was 12 to 15 and should probably be more appropriately called oligomers.



The infrared spectra of the soluble fractions could be superimposed on the spectra of the insoluble fractions except in the 3100-3500  $\text{cm}^{-1}$  region where a medium intensity broad absorption was observed for the soluble fraction. After this fraction was endcapped this broad band was absent and a carbonyl band at 1700  $\text{cm}^{-1}$  due to the acetyl carbonyl in the end groups was present. The intensity of this carbonyl band was compared to the intensity of a carbonyl band in a polyaldehyde-polyvinylacetate mixture of known composition. The relative intensity of the carbonyl band in the endcapped polyaldehyde, using this mixture as a reference, also indicated at  $\text{DP}_n$  of 12 to 15.

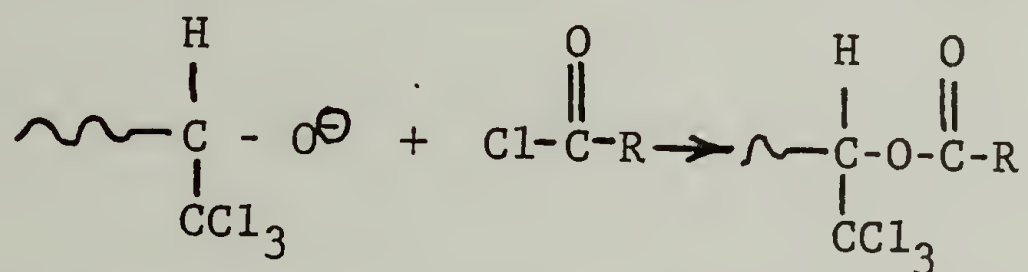
To summarized then, the homopolymers of BDCA, CDBA, and bromal were insoluble in all solvents tested. Oligomers of BDCA soluble in  $\text{CH}_2\text{Cl}_2$  were isolated in two cases.

#### Molecular Weights Determination

The homopolymers of BDCA, CDBA and bromal were insoluble in all organic solvents tested. An oligomer of bromodichloroacetaldehyde was isolated and because it was soluble in several organic liquids it could be end capped with acetic anhydride under acidic conditions. A number

average molecular weight of 4500 was obtained by vapor phase osmometry for the oligomer. The insoluble homopolymers, prepared under anionic and cryotachensic conditions, could not be end capped by treatment with acetic anhydride or acetyl chloride. A previously developed method for the molecular weight determination of polychloral was used to estimate the minimum molecular weights of the homopolymers of BDCA, CDBA and bromal.

According to this method of growing oxyanion in an anionic chloral polymerization reacts with an acid chloride to yield an acylated polymer with an ester end group.



The molecular weights of the polymers were estimated by determining the concentration of ester end groups. The intensity of the ester carbonyl absorption in the infrared region was  $1770 \text{ cm}^{-1}$  was compared to the intensities of the ester absorption in polyaldehyde-polyvinylacetate mixtures of known composition. The minimum number average molecular weights by end groups analysis for the homopolymers of BDCA, CDBA and bromal are presented in

Table 16.

TABLE 16

MOLECULAR WEIGHTS OF HOMOPOLYMERS DETERMINED BY  
ENDGROUP ANALYSIS BY INFRARED SPECTROSCOPY

Monomer	Initiator	Dp <sub>n</sub>
BDCA	Pyridine	115
BDCA	SbCl <sub>5</sub>	80
CDBA	Pyridine	95
CDBA	SbCl <sub>5</sub>	80
Bromal	Pyridine	55

The polymers prepared in the presence of acid could be end capped by treatment with refluxing acetic anhydride. The concentrations of the ester end groups for these polymers were also estimated by the infrared technique. The polymers prepared under acid conditions were apparently less crystalline or had end groups which were more accessible for end capping. The molecular weights of these polymers were slightly lower than the molecular weights of the polymers prepared with pyridine.

### Wide Angle X-ray Diffraction and Crystallinity

The wide angle x-ray diffraction patterns of the homopolymers of  $\text{Cl}_2\text{CBrCHO}$ ,  $\text{Br}_2\text{CClCHO}$ , and  $\text{Br}_3\text{CCHO}$  show sharp lines. The photographs closely resemble x-ray diffraction patterns of polychloral. The photographs are shown in Appendix 4.

The homopolymers of chloral, BDCA, CDBA and bromal prepared with pyridine as the initiator showed sharp and very similar diffraction lines. The prominent lines and their spacing are listed in Table 17 (page 243).

The five strongest lines present in the polychloral pattern are also present in the other two patterns in nearly the same spacings. There was a slight increase in the spacing with increasing bulk of the side chain but the increases which are due to increases in interchain distances are very small indeed. The similarities however indicate that the homopolymers have similar structures.

Polybromal has a generally similar diffraction pattern with the longer spacing, which would be expected for a polymer with a bulkier side group.

X-ray diffraction patterns of the homopolymers varied.



TABLE 17

INTERPLANAR SPACINGS OF POLYCHLORAL AND  
CCl<sub>2</sub>BrCHO, Br<sub>2</sub>CCl CHO, and BROMAL HOMOPOLYMERS (Å)

Poly Chloral Spacing Approx. Intensity	Poly C12CBrCHO Spacing Approx. Intensity	Poly Br2CC1CHO Spacing Approx. Intensity	Poly Br3CCHO Spacing Approx. Intensity
8.70	100	8.80	100
5.00	90	5.10	90
3.30	60	3.40	60
2.73	50	2.75	50
2.40	40	2.35	40
		8.90	100
		5.10	90
		3.40	60
		2.80	50
		2.30	40
		9.30	100
		5.40	90
		3.60	100
		2.80	30

### Low Angle Light Scattering and Morphology

Films of polychloral and polybromodichloroacetaldehyde prepared by monomer casting under anionic conditions were found to exist in a rodlike morphology according to low angle polarized light scattering. The Hv (analyzer horizontal, polarizer vertical) light scattering pattern showed a maximum in scattering intensity at  $0^\circ$  with intensity decreasing with increasing  $\theta$ . The cross pattern has been observed for many other polymers such as polytetrafluoroethylene containing a rodlike morphology.<sup>(151)</sup> The cross pattern was observed for both polychloral and poly  $\text{Cl}_2\text{C Br CHO}$ . The orientation of the cross was  $45^\circ$  to the cylinder axis. The Hv patterns resembled closely the Hv pattern for polytetrafluoroethylene which is known to have this rodlike superstructure.

The Vv patterns were circular in shape. Density fluctuations are aximuthal independent while fluctuations in directional orientation of the rod optic axis depended on the aximuthal angle. Both fluctuations contribute to Vv scattering. The Vv scattering arose from density

fluctuations for these two homopolymers since no angular dependence was observed.

The Vv pattern was much more intense than the Hv pattern. The Vv scattering arose from density fluctuations, and this type of fluctuation was much more pronounced than fluctuations in directional orientation (Hv). The polymer superstructures consisted therefore of some amorphous regions and the rod-structure was not volume filling. Swelling of the polymers with ortho-dichlorobenzene appeared to have little effect on the observed scattering patterns. The homopolymers of chloral and  $\text{Cl}_2\text{CBr CHO}$  had a rodlike morphology with some amorphous regions and the polymer chain axis was oriented at  $45^\circ$  to the rodlike superstructure. Helices were probably stacked together at  $45^\circ$  with respect to the crystallite.

Spherulite and disc like morphologies are ruled out because they show very different Hv and Vv patterns.

#### End Capping and Chemical Stability of BDCA, CDBA, and Bromal Homopolymers

The homopolymers of  $\text{Cl}_2\text{CBr CHO}$ .  $\text{Br}_2\text{CCl CHO}$  and

$\text{Br}_3\text{C CHO}$  could be stabilized by treatment with  $\text{PCl}_5$  in  $\text{CCl}_4$ , which had been used to stabilize polychloral.<sup>(94)</sup> The degree of stabilization of the homopolymers could be determined by differential thermal analysis. The DTA curves are shown in Appendix 3. The temperature of the maximum degradation rate was markedly higher for each homopolymer than for the raw polymers. However, it is not known what unstable end group was replaced by this treatment nor which stable end groups were introduced.

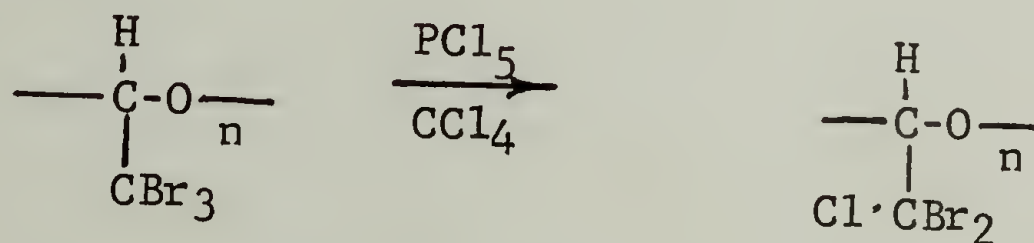
Some polymers of BDCA, CDBA, and bromal contained weak absorptions near  $3200$  to  $3600\text{ cm}^{-1}$  in their infrared spectra prior to treatment with  $\text{PCl}_5$  and contained no absorptions in the  $3200\text{ cm}^{-1}$  to  $3600\text{ cm}^{-1}$  region after treatment. Therefore the stabilization was probably a replacement of an OH end group with a chloride end group.

Hydroxyl terminated polymeric aldehydes, including polyformaldehyde are known to be unstable and to degrade quantitatively to monomer by an unzipping reaction. These polymers can be stabilized by treatment with acetic anhydride which converts hydroxyl end groups to stable ester end groups. It was not possible to stabilize the



homopolymers of  $\text{Cl}_2\text{CBr CHO}$ ,  $\text{Br}_2\text{CCl CHO}$  and  $\text{Br}_3\text{C CHO}$  prepared under cryotachensic anionic conditions with acetic anhydride or acetyl chloride but these homopolymers could be successfully stabilized by  $\text{PCl}_5$  treatment.

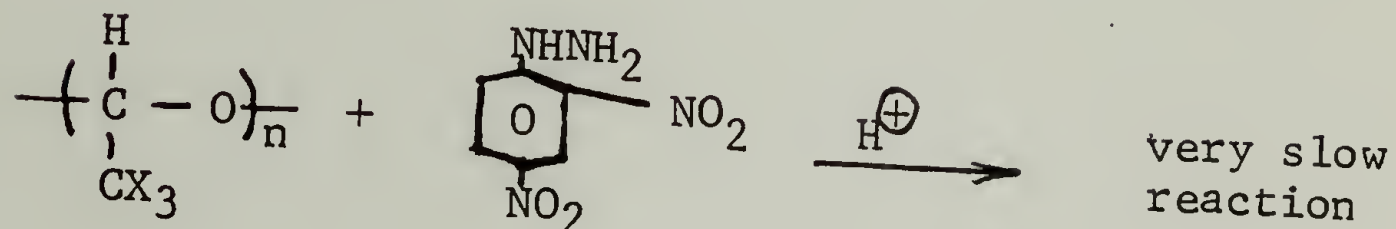
The polymer treatment with  $\text{PCl}_5$  did not attack the substituent groups on the polymer chain. A careful examination of the infrared spectrum of each homopolymer revealed that there was no exchange of chlorine for bromine.



The infrared spectra in the carbon halogen stretch region,  $900\text{--}250\text{ cm}^{-1}$ , were identical before and after treatment.

Most aliphatic aldehyde polymers are degraded rapidly by strong acids and by the standard 2,4 dinitrophenylhydrazine reagent in ethanol and sulphuric acid.<sup>(155)</sup> The stability of the homopolymers of  $\text{Cl}_2\text{CBr CHO}$ ,  $\text{Br}_2\text{CCl CHO}$ , and  $\text{Br}_3\text{C CHO}$  in strong acid and in 2,4 dinitrophenylhydrazine reagent was determined, but these stabilized homopolymers were attacked very

slowly by 6N  $\text{H}_2\text{SO}_4$ , even after two weeks and by the 2,4 dinitrophenylhydrazine reagent only after a period of ten days.



These four homopolymers stabilized by treatment with  $\text{PCl}_5$  in  $\text{CCl}_4$  were inert toward bases. Pyridine, lithium tertiary butoxide in methyl cyclohexane, sodium methoxide in hexamethylphosphorous triamide, and potassium iodide in acetone failed to degrade these polymers after 8 hours at  $25^\circ\text{C}$ . The polymers were recovered quantitatively.

#### G. Copolymer Characterization

##### Copolymers with Chloral

Copolymers of chloral and bromal, chloral and BDCA, and chloral CDBA were characterized by infrared

spectroscopy TGA, DSC, low angle light scattering and vacuum degradation. The characterization studies indicated that these compounds were true copolymers and not homopolymer mixtures. All of the copolymers of high molecular weight were insoluble. The properties of these copolymers and the evidence for true copolymers are discussed below.

#### Vacuum Degradation

The copolymer compositions for the systems chloral/BDCA, chloral CDBA and chloral/bromal were calculated from the data obtained from the vacuum degradation of each copolymer. The copolymers were degraded thermally in sealed tubes and the volatile products were analyzed by gas chromatography. The percent of each monomer was determined by measuring the area for each monomer in the chromatogram. In Table 18 the copolymer compositions are given along with the ratios of the monomers in the feed in the cationic polymerizations. Table 18 contains the feed and copolymer composition data for the experiments where pyridine was the initiator.

TABLE 18

$\text{Cl}_3\text{CCHO}/\text{Cl}_2\text{CBrCHO}$  Copolymer Compositions  
(Initiator:  $\text{CF}_3\text{SO}_3\text{H}$ ; 2 mole %; Bulk Polymerization)

Comonomer	% Chloral in Feed	% Chloral in Copolymer
BDCA	75	82
	50	58
	25	31
CDBA	75	86
	50	64
	25	46
Bromal	75	100
	50	100
	25	100

TABLE 19

Chloral/BDCA and Chloral/Bromal CoPolymer Compositions  
(Initiator: Pyridine; Initiator Concentration: 2.0 mole %; 20% Toluene Diluent)

Percent Chloral in Feed	Comonomer	Percent Chloral in Copolymer
75%	BDCA	90
50%		75
25%		54
75%	CDBA	95
50%		88
25%		72
75%	Bromal	100
50%		98
25%		98



The data in Tables 18 and 19 show that in copolymerizations in the presence of acid chloral, BDCA and CDBA were much more reactive than bromal. Under anionic conditions at  $-78^{\circ}\text{C}$  chloral was more reactive than CDBA. Bromal was very unreactive under any conditions.

### Infrared Spectra

BDCA/chloral copolymers had infrared spectra containing narrow sharp lines in the region  $1400\text{--}1300\text{ cm}^{-1}$  and near  $2940\text{ cm}^{-1}$ . At  $2940\text{ cm}^{-1}$  only one narrow line was observed and between  $1400\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$  only two sharp lines were observed. These lines correspond to C-H stretching and C-H bending motions. Only one kind of C-H bond was present in the copolymer. A 1 to 1 mixture of the homopolymers of chloral and BDCA had 4 lines on the region  $1300\text{--}1400\text{ cm}^{-1}$  and two lines in the  $2940\text{ cm}^{-1}$  region. Two separate homopolymers mixed together showed distinct and separate C-H bonds. The infrared spectrum of the mixture in the  $900\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  region looked like a superposition of two infrared spectra of the homopolymers. The copolymer however had a spectrum in

this region which was different from each homopolymer spectrum and which was not a simply superposition of the two. The copolymer was probably a true copolymer and not a simple mixture of the homopolymers of chloral and BDCA.

In other regions of the infrared spectrum, particularly in the region  $1200\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  where the carbon-oxygen single bond stretching bands occur, the copolymer spectrum closely resembled the homopolymer spectra. The same kinds of infrared active motions took place and therefore the copolymer was probably a helical structure like polychloral. The two groups  $-\text{C Cl}_3$  and  $\text{CBrCl}_2$  could be accommodated in the same helix.

Furthermore infrared spectra of chloral - CDBA copolymers showed sharp single lines at  $2940\text{ cm}^{-1}$ ,  $1350\text{ cm}^{-1}$ . Mixtures of the homopolymers of chloral and CDBA showed two lines near  $2940\text{ cm}^{-1}$ , two lines near  $1350\text{ cm}^{-1}$  and two lines near  $1310\text{ cm}^{-1}$ .

The infrared spectra of the chloral-bromal copolymers could be nearly superimposed on the spectra of chloral homopolymers particularly in the region  $900\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$ . A weak band at  $630\text{ cm}^{-1}$  where a carbon

bromine stretching motion would be expected was observed. This band was not present in extracted samples showing that they were pure polychloral according to infrared spectra. The conclusion is that bromal cannot easily be accommodated in the polychloral chain. Polybromal can apparently form its own helix but the bulky  $\text{CBr}_3$  group cannot enter the polychloral chain with the same ease that the  $\text{CCl}_2\text{Br}$  and  $\text{Br}_2\text{CCl}$  group can.

### Thermal Analysis

The DTG curves for copolymers of chloral and BDCA and for the copolymers of chloral and CDBA prepared under anionic conditions each showed one maximum and not two or more maxima, but a mixture of two homopolymers showed the two different maxima of each homopolymer.

The DTG curves for the copolymer prepared by cationic initiators, shown in Appendix 3, had maxima at high temperatures. These copolymers were more stable than the copolymers prepared under anionic conditions. Several maxima were observed in the DTG curves and chars remained from these copolymers prepared under acid conditions. Copolymers prepared under anionic conditions

and not treated with  $\text{PCl}_5$  or acetic anhydride, degraded completely without leaving any char. The DTG data is summarized in Table 20.

Analysis by Differential Scanning Colorimetry

TABLE 20

DTG MAXIMA FOR ALDEHYDE COPOLYMERS  
Heating Rate  $20^\circ\text{C}/\text{Min.}$

Copolymer	Initiator	Maxima
BDCA/Chloral	Pyridine	144
BDCA/Chloral	$\text{CF}_3\text{SO}_3\text{H}$	249
CDBA/Chloral	Pyridine	125
CDBA/Chloral	$\text{CF}_3\text{SO}_3\text{H}$	250

The DSC curves for the copolymers in the temperature range of  $-80^\circ\text{C}$  to the polymer decomposition temperatures did not reveal any transitions.

Copolymers with Isocyanates

The copolymers of BDCA, CDBA and bromal, with phenyl isocyanate and n-butyl isocyanate were formed under anionic conditions and the polymerizations were gel



forming. The amount of isocyanate incorporated in the copolymer chain varied considerably with the structure of the aldehyde and the isocyanate.

### Elemental Analysis

The copolymer compositions for the aldehyde-isocyanate copolymers were determined by elemental analysis for nitrogen. The analysis and the percent isocyanate is shown for each copolymer in Table 21 (page 256). The data in the table indicate that the order of reactivity of the aldehydes with isocyanates in copolymerization decreases with increasing side group size of the aldehyde. Much more phenyl isocyanate was present in the copolymer of bromal than in the polybromodichloroacetaldehyde chain when 10 percent of the isocyanate was present in the feed. The bromal-phenyl isocyanate copolymerization yielded a copolymer that was very nearly a 1 to 1 copolymer when the phenyl isocyanate was in slight excess in the feed. The reactivity of  $\text{Cl}_2\text{CBrCHO}$  was therefore higher in isocyanate copolymerizations and less isocyanate was incorporated. The reactivity of

TABLE 21

## COMPOSITION OF ALDEHYDE--ISOCYANATE COPOLYMERS

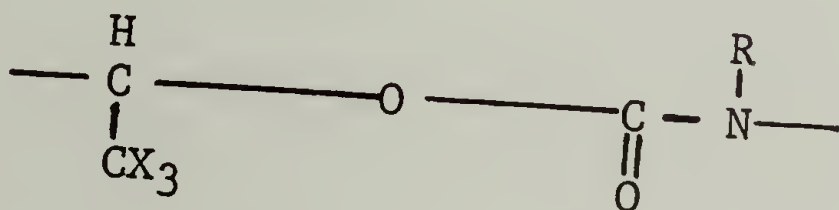
	% Isocyanate in Feed	Analysis for N	% Isocyanate in Product
BDCA-PhNCO	5	0.62	7
	10	1.23	13
	20	1.45	16
	50	2.87	32
CDBA-PhNCO	5	0.58	7
	10	1.02	13
	20	2.11	27
	50	2.96	38
Bromal-PhNCO	5	0.54	7.8
	10	0.77	11.0
	20	1.24	17.7
	50	3.02	43.1, 44.2
	55	3.46	50.0
BDCA-M-butyl- NCO	50	0.58	4.6
CDBA-M-butyl- NCO	50	0.68	10.0
Bromal-M-butyl- NCO	50	0.45	6.4
Bromal-p- CH <sub>3</sub> Ph·NCO	50	1.15	16.4

bromal was so low at  $-78^{\circ}$  that a nearly 1:1 copolymer was formed.

The data in Table 21 also indicate that n-butyl isocyanate and paramethylphenyl isocyanate were much less reactive than phenyl isocyanate. The aliphatic isocyanate was incorporated to a small extent in all copolymerizations.

### Infrared Spectra

An absorption at 5.75  $\mu$  in all of the copolymer spectra indicated the presence of a urethane link in the molecule.



The intensity of this band was closely related to the isocyanate content in the copolymer (according to the analysis for nitrogen) and the spectra closely resembled spectra of chloral isocyanate copolymers. Changes in the spectra with increasing isocyanate content in the region of 1400 to 900  $\text{cm}^{-1}$  were observed in the copolymers, and in a set of standard chloral phenylisocyanate copolymers

of known composition.

The carbon hydrogen bending lines near  $1320\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  were unchanged in position but slightly in intensity when small amounts of isocyanate were present. The carbon-oxygen ether bands around  $1100\text{ cm}^{-1}$  were also affected very little by small amounts (up to 10%) of isocyanate in the chain. The internal order of the chain was not affected. The urethane links and the phenyl groups did not seriously distort the conformation of the polyaldehyde chain until the isocyanate content reached about 10%. For the copolymers containing more than 10 percent isocyanate the infrared spectra changed rapidly in the  $1400\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  region with increasing isocyanate content. The lines in the region of  $850\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  were not shifted but changed in intensity linearly in copolymers with high isocyanate content. These bands are due to carbon halogen stretching motions and are not greatly affected because the halogen atoms are not bonded directly to the polymer backbone.



### Thermal Gravimetric Analysis

The DTA curves for the isocyanate-Perhaloacetaldehydes copolymers are shown in Appendix 2 and the maxima in the degradation rates are listed in Table 22.

TABLE 22

DTG MAXIMA FOR ALDEHYDE-ISOCYANATE COPOLYMERS °K  
Heating Rate: 20°C/Min.

Copolymer	% Isocyanate in Copolymer	Temperature of maximum degradation rate		
		T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>
BDCA	13.7	220	304	
	16.1	218	323	
	31.9	238	298	
CDBA-PhNCO	7.5	232	323	
Bromal-PhNCO	7.8	220	248	296
	50	257		
Bromal-CH <sub>3</sub> PhNCO	16.4	255	288	

The data in the table indicate that the copolymers were much more thermally stable than unstabilized homopolymers which were prepared by anionic initiation. The urethane link prevented an unzipping of the polyaldehyde chain from unstable groups. Several maxima were sometimes present in the DTA curves. The ultimate stability

of these polymers are not as high as stabilized homopolymers which indicated that the urethane link is not as stable as polyoxymethylene backbone. After degradation of the isocyanate copolymers a char always remained.

#### Differential Scanning Calorimetry

In the temperature range of  $-80^{\circ}\text{C}$  to just below the copolymer decomposition temperature the DSC data did not provide evidence for a glass transition or a melting point for any of these copolymers. Even the bromal phenyl isocyanate 1 to 1 copolymer did not appear to have a  $T_g$  or  $T_m$  below the decomposition temperature.

#### Wide Angle X-ray Scattering

The wide angle x-ray diffraction patterns of the 3 copolymers of BDCA, CDBA and bromal with phenyl isocyanate (the isocyanate content was about 10% in each copolymer) showed broad lines indicating that crystallinities of these copolymers were less than the crystallinities of the homopolymers. The soluble bromal phenyl isocyanate 1/1 copolymer however gave sharp lines in its x-ray diffraction pattern. The spacings were unique and they

had no resemblance to the spacings in the bromal homopolymer pattern. The 1:1 copolymer is therefore a highly ordered structure which would be expected if the 1/1 copolymer were perfectly alternating.

### Low Angle Light Scattering

Films of a chloral-O-chlorophenyl isocyanate copolymer and a BDCA-phenyl isocyanate copolymer, each containing 5% isocyanate, were analyzed by low angle polarized light scattering. The cross observed in the Hv photograph of the homopolymer films was not present in the copolymer photographs. The Hv scattering of the copolymer was featureless and the rodlike morphology which was present in polychloral and polybromodichloroacetaldehyde present in the isocyanate copolymers and indicated the absence of a rodlike superstructure. The Vv patterns were circularly symmetric and very intense. The Vv scattering arose from density fluctuations primarily and not from fluctuations in directional orientation of a rod optic axis. The rods were very small if they were present.



### Solubility and NMR Spectrum

The bromal-phenyl isocyanate 1:1 copolymer was the only copolymer that was soluble in some organic solvents. Dichloromethane was the best solvent ( $\delta = 9.7$ ). An NMR spectrum of this copolymer is shown in Appendix 1. One broad signal extending from 6.68 to 7.18 roughly Gaussian in shape was the only signal observed. A line between 5 and 6 PPM which would be expected for a polybromal acetal proton was not observed. This seems to suggest that the copolymer is completely alternating with only urethane linkages in the polymer chain.

The proton of the urethane linkage was probably part of the broad peak which was produced by the phenyl protons.

### Molecular Weight

The number average molecular weight for the bromal phenyl isocyanate 1:1 copolymer was about 7000 by vapor phase osmometry. Chloral isocyanate copolymers containing more than 30% isocyanate are also soluble and have been reported to be low in molecular weight.



## H. Miscellaneous Experiments

### 1. Polymerization of $\text{Cl}_3\text{CHO}$ and $\text{Cl}_2\text{CBrCHO}$ in Highly Solvating Media

A series of experiments were designed to determine the effect of a highly solvating solvent on the stereoregularity of the polymerization of chloral and BDCA. Dimethyl sulfoxide, a solvent of good solvating power, was selected for these experiments. Pyridine and trimethylamine were the initiators for anionic polymerization of chloral and BDCA in DMSO. The initiators were added to the monomer solutions which were maintained above the polymerization temperatures and the solutions polymerized by cooling in a bath of  $-10^\circ\text{C}$  and  $-40^\circ\text{C}$ . The polymerizations proceeded rapidly but the rates were slower than typical bulk polymerizations. Homogeneous waxes were formed in every case and they were polymer swollen with DMSO. The DMSO partially solvated the chains to produce the translucent waxes; addition of any solvent caused a partial precipitation of the product. The reaction conditions and yields are given in Table 23.

TABLE 23

ALDEHYDE POLYMERIZATION OF CHLORAL AND BDCA IN DMSO  
Reaction Time: 16 Hrs.

Monomer	Initiator 2 mole %	Monomer Concen- tration in DMSO	T bath <sup>o</sup> C Reaction	Product Yield
Chloral	Pyridine	5M	-10 <sup>o</sup>	63
Chloral	Pyridine	3M	-10 <sup>o</sup>	42
Chloral	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	5M	-10 <sup>o</sup>	68
Chloral	(C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub> N	3M	-10 <sup>o</sup>	45
BDCA	Pyridine	5M	-30 <sup>o</sup>	50
BDCA	Pyridine	3M	-30 <sup>o</sup>	38
BDCA	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	5M	-30 <sup>o</sup>	52
BDCA	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3M	-30 <sup>o</sup>	38
Chloral	No initiator	5M	-10 <sup>o</sup>	53

An infrared spectrum of each reaction product was taken. All of the infrared spectra of the reaction products could be superimposed on previous infrared spectra of Cl<sub>3</sub>CCHO and BDCA homopolymers. These products could be stabilized by treatment with PCl<sub>5</sub> in CCl<sub>4</sub>. The reaction products were insoluble in all solvents when attempts were made to dissolve the precipitated polymers. The polymers were nearly amorphous according to their

wide angle x-ray diffraction diagrams.

We concluded from these experiments that according to I.R. spectra, the polymers were still isotactic like the polymers prepared in bulk and in poorly solvating solvents.

DMSO initiated the polymerization of chloral without added tertiary amines. The polymerization was much slower than polymerizations with added initiator. The spectrum of this polymer was also the same; consequently, the polymer stereochemistry was also identical to polymers obtained previously.

Chloral and  $\text{Cl}_2\text{CBrCHO}$  each polymerized in nitrobenzene, a solvent with a high dielectric constant, a good solvent for cationic polymerizations in the presence of  $\text{CF}_3\text{SO}_3\text{H}$  to form polymers. I.R. spectra could be superimposed on I.R. spectra of polymers prepared in bulk with pyridine. As the initiator, the yields were considerably higher for polymerizations with  $\text{CF}_3\text{SO}_3\text{H}$  initiation in nitrobenzene (50%) than for bulk polymerizations with  $\text{CF}_3\text{SO}_3\text{H}$  initiation of chloral and BDCA (30%). These polymerizations in highly solvating or high dielectric

constant solvents yielded isotactic polymers only.

2. Crystallinity and Selective Degradation by Secondary Amines.

Piperidine and other secondary amines degraded chloral dichloroacetaldehyde copolymers which were not stabilized. (157) Secondary amines and primary amines were the only compounds that quantitatively degraded these copolymers.

It was postulated that secondary amines in dichloromethane would penetrate the amorphous regions of polychloral and degrade the polymer only in these regions without penetrating and degrading the crystalline regions. An independent measure of crystallinity would be possible if this selective degradation took place.

The results of this experiment on several homopolymers are shown in Table 24 (see p. 267). The polymers were exposed to piperidine in dichloromethane for 24 hours at 25°C. The results were reproducible for samples of polymer prepared with a given initiator. The weight of each sample remained constant after 24 hours.

The piperidine degraded the polychloral which had



TABLE 24

## EFFECT OF PIPERIDINE ON HOMOPOLYMERS

Sample	Initiator used for Preparation	% Weight Loss	% Cryst.
$\left( \begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} \\   \\ \text{CCl}_3 \end{array} \right)_n$	$\text{Ph}_3\text{P}$	49.3	50.7
$\left( \begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} \\   \\ \text{CCl}_3 \end{array} \right)_m$	Pyridine	50.4	49.6
$\left( \begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} \\   \\ \text{CCl}_3 \end{array} \right)_n$	Li Tert Butoxide	45.1	54.9
$\left( \begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} \\   \\ \text{CCl}_3 \end{array} \right)_n$	$\text{H}_2\text{SO}_4$	77.0	23.0
$\left( \begin{array}{c} \text{H} \\   \\ \text{C} - \text{O} \\   \\ \text{BRCCl}_2 \end{array} \right)_m$	Pyridine	53.4	46.6

been prepared from chloral and  $\text{H}_2\text{SO}_4$  to the greatest extent. This sample was nearly amorphous according to wide angle x-ray scattering. In contrast the other polychloral samples prepared from chloral and an anionic initiator were more stable. These anionic polymers were semi-crystalline according to wide angle x-ray scattering.

Recently a correlation between tensile modulus and percent crystallinity was published. (156)

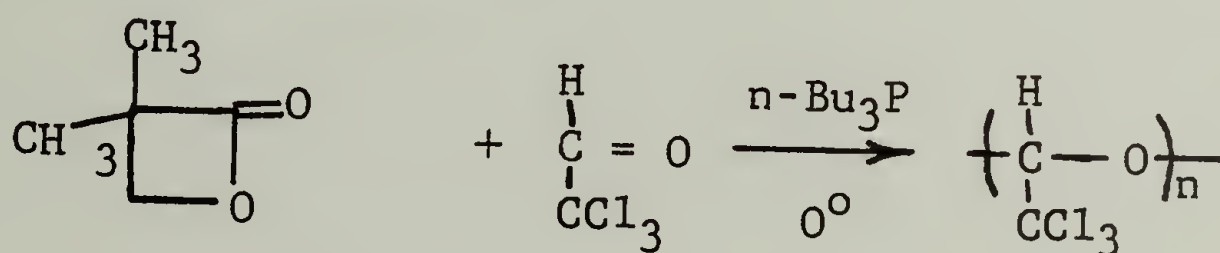
$$G_{\text{obs}}^{1/5} = \phi_1^{1/5} G_1 + \phi_2^{1/5} G_2$$

Where  $G_{\text{obs}}$  is the observed modulus and  $G_1$  = modulus of an isotropic amorphous phase and  $G_2$  is the modulus of the crystalline phase. The values of  $G_1$  has been assumed to be  $2 \times 10^6$  dyne/cm<sup>2</sup>. If the published value of 4800 psi =  $3.32 \times 10^8$  dyne/cm<sup>2</sup> is used for  $G_{\text{obs}}$  then  $\phi_1 = 0.46$  or the percent crystallinity is equal to 54%. The values for the percent crystallinity according to the modulus, x-ray data, and piperidine degradation data are fairly close. The conclusion of this experiment is that crystallinity of an aldehyde homopolymer might be measured by a unique method involving the degradation of the amorphous

regions by some compound that will induce unzipping. Polychloral has a rodlike morphology with some amorphous regions and a percent crystallinity may represent the percent of the volume that is filled with well organized rods.

3. The Reaction of Chloral, Pivalolactone and Tri(n-butylphosphine).

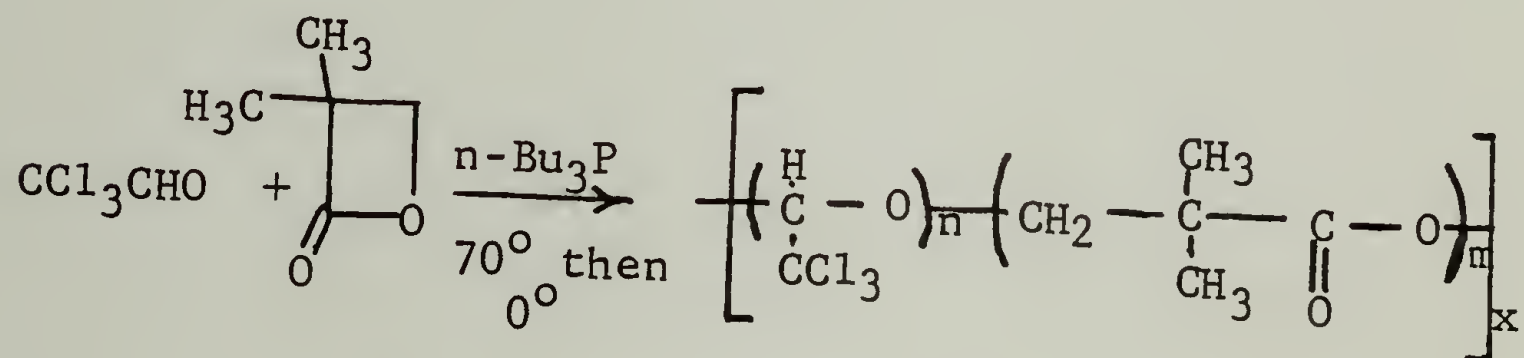
A 1:1 mixture of chloral and pivalolactone was reacted with 1 mole percent tri(n-butylphosphine) in three separate experiments. In the first experiment, the tri(n-butylphosphine) was added at 0°C and a solid product formed within one hour. This product was isolated and purified. Its infrared spectrum could be superimposed on previous spectra for polychloral.



In the second experiment, tri(n-butylphosphine) was added at 70°C to the 1:1 mixture. The mixture was maintained at 70°C for one hour. Polypivalolactone oligomer was isolated from this reaction mixture as the only solid product. The I.R. spectrum could be superimposed or

published spectra for polypivalolactone.

In the third experiment, tri(*n*-butylphosphine) was added at 70°C to the 1:1 mixture and the mixture was then cooled in a bath to 0°C for one hour. A solid block of polymer was isolated in 65% yield which was insoluble in acetone and trifluoroacetic acid. The I.R. spectrum of this product showed absorptions of polychloral polypivalolactone, and additional absorptions.



This product was either a copolymer of chloral and pivalolactone with blocks or an intimate blend of the two homopolymers. The analysis for chlorine indicated that this polymer had a composition of nearly 1:1.

#### 4. Attempted Copolymerization of Chloral with Acrylonitrile and of Bromal with Acrylonitrile under Anionic Conditions

Polar olefins with electron withdrawing substituents are known to polymerize under anionic conditions.



Relatively weak nucleophiles have been reported to initiate the polymerization of acrylonitrile. In this set of experiments, an attempt was made to determine whether acrylonitrile would copolymerize with chloral or bromal under reaction conditions used for the aldehyde homopolymerizations. Acrylonitrile was used as a potential comonomer and the polymerization was carried out with chloral and with bromal by cryotachensic polymerizations.

Chloral homopolymerized in the presence of acrylonitrile with pyridine as the initiator used. Polychloral gels were formed and the yields of polychloral were about 50%. I.R. spectra of the products could be superimposed in the spectra of chloral homopolymers. No other polymeric products could be detected and no polyacrylonitrile was formed. Bromal also homopolymerized in the presence of this acrylonitrile. Acrylonitrile simply acted as an inert diluent.

The failure of the polychloral anion or the polybromal anion to initiate the polymerization of acrylonitrile was probably due to the low nucleophilicity of the oxyanion.

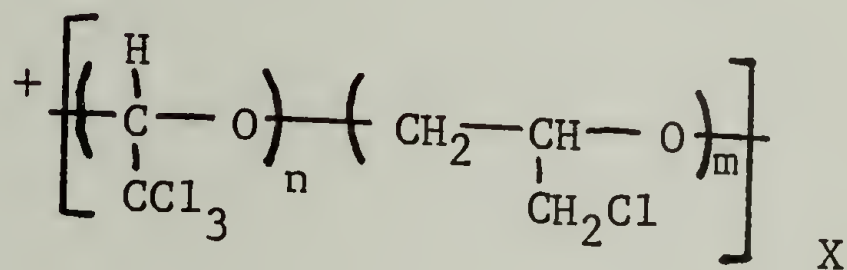
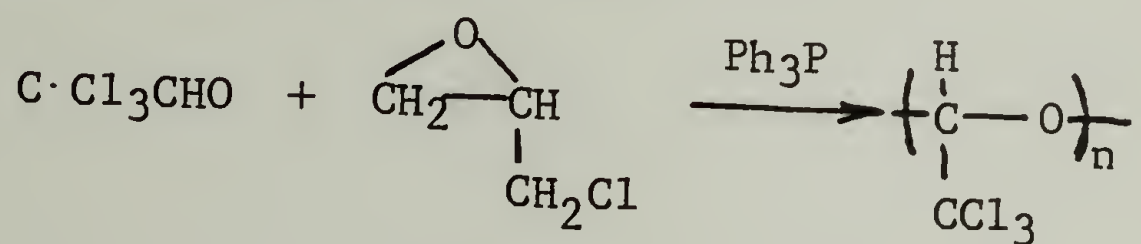
5. Reaction of Trioxane, Bromal and Antimonypentachloride

Trioxane homopolymerized in excess bromal in the presence of  $\text{SbCl}_5$  at  $35^\circ\text{C}$ . An infrared spectrum of the isolated product could be superimposed on a l.R. spectrum of polyoxymethylene. Bromine was absent in the product according to elemental analysis. A soluble copolymer of trioxane and bromal could not be isolated from the reaction.

6. Reaction of Chloral, Epichlorohydrin, and Triphenylphosphine

Chloral, epichlorohydrin, and the nucleophile triphenylphosphine were mixed at  $70^\circ\text{C}$  and were injected, by monomer casting, between glass plates to form a film of polymer. The polymerization was very rapid at  $0^\circ\text{C}$ . The product contained a fraction that was stable at  $120^\circ\text{C}$ . This product had an l.R. spectrum that contained all of the polychloral lines and many other lines including a band in the saturated carbon hydrogen stretch region. Analysis for chlorine indicated that this product had less chlorine than theory for polychloral. This stable fraction represented  $1/3$  of the total product. The remainder

was unstable at 120°C and degraded to monomeric chloral after 48 hours. The product contained polychloral and a second fraction which may have substituted ethylene oxide units which stabilized this fraction.



### CONCLUSIONS

1. BDCA, CDBA, and bromal polymerized in the presence of nucleophiles and certain acids to form insoluble semi-crystalline substituted polyoxymethylenes. The elemental analysis, I.R. spectra, thermal degradations and wide angle x-ray diffraction patterns suggested that these homopolymers closely resembled isotactic polychloral when they were prepared in bulk, in low dielectric constant solvents, and in high dielectric constant solvents under anionic and cationic conditions. The size of the trihalomethyl groups caused steric crowding in the growing polymer chains which permitted monomer addition in only one stereospecific way in the meso configuration to form isotactic polymers. Stereoregular polymers were obtained without the use of stereospecific or stereoelective initiators in every case where the side group was as large or larger than the trichloromethyl.
2. BDCA was more reactive than CDBA which was more reactive than bromal since the threshold temperatures



were found to be  $-11^{\circ}\text{C}$  (BDCA),  $-43^{\circ}\text{C}$  (CDBA) and  $-75^{\circ}\text{C}$  (bromal). These threshold polymerization temperatures decrease with successive substitution of bromine for chlorine and successive increase in side group size. For polymerizations in the presence of nucleophiles, good conversions were obtained for all 3 monomers, but in the presence of acids, CDBA and bromal were much less reactive than BDCA.

3. Homopolymers of BDCA, CDBA, and bromal (like polychloral) prepared under anionic conditions degraded quantitatively to monomer around  $150^{\circ}\text{C}$  but they could be stabilized by treatment with  $\text{PCl}_5$  up to  $250^{\circ}\text{C}$ . The homopolymers prepared in the presence of acids contained fractions with different end groups and several maxima were observed above  $200^{\circ}\text{C}$  in the DTG curves.
4. X-ray scattering patterns for homopolymers of BDCA, CDBA, and bromal closely resembled the x-ray patterns for polychloral. Low angle light scattering patterns for polychloral and for polybromodichloroacetaldehyde indicated the presence of a rodlike morphology and

some amorphous regions and the absence of spherulites. The structure and morphology for all homopolymers were very similar, regardless of the initiator used in their preparation.

5. No transitions,  $T_g$ , or  $T_m$ , were observed for stabilized homopolymers of BDCA, CDBA, and bromal below the decomposition temperatures.
6. CDBA, BDCA, and bromal copolymerized with isocyanates and with chloral. The isocyanate copolymers were similar to chloral-isocyanate copolymers in solubility behavior, crystallinity, and thermal stability. Bromal was more reactive than CDBA which was more reactive than BDCA in copolymerizations with isocyanates. The copolymers of CDBA, BDCA, and bromal with chloral were probably helical and were very similar to the homopolymers of these monomers. The bulky side groups caused steric hinderance which allowed successive stereospecific addition during copolymerization with chloral.

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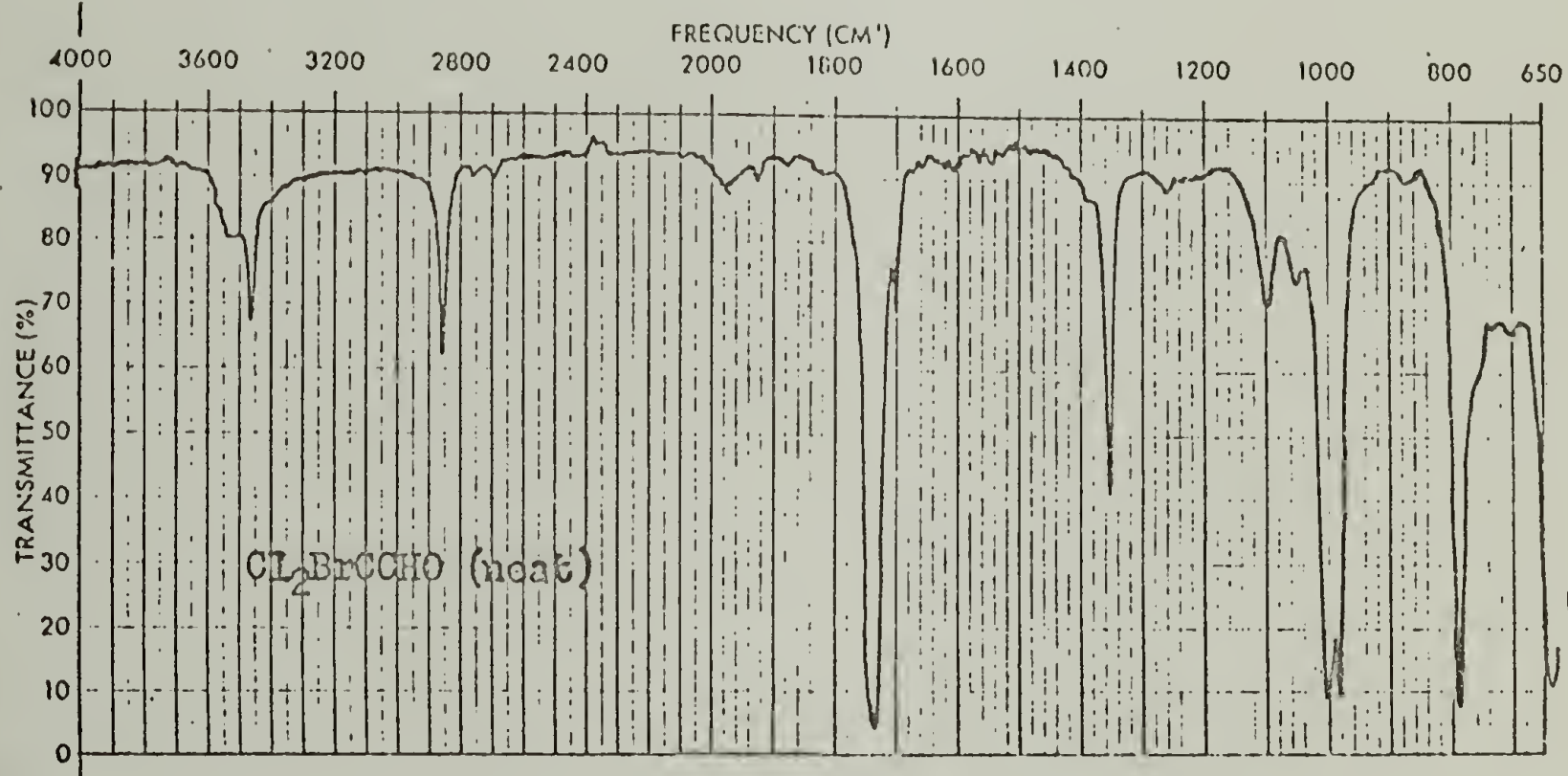


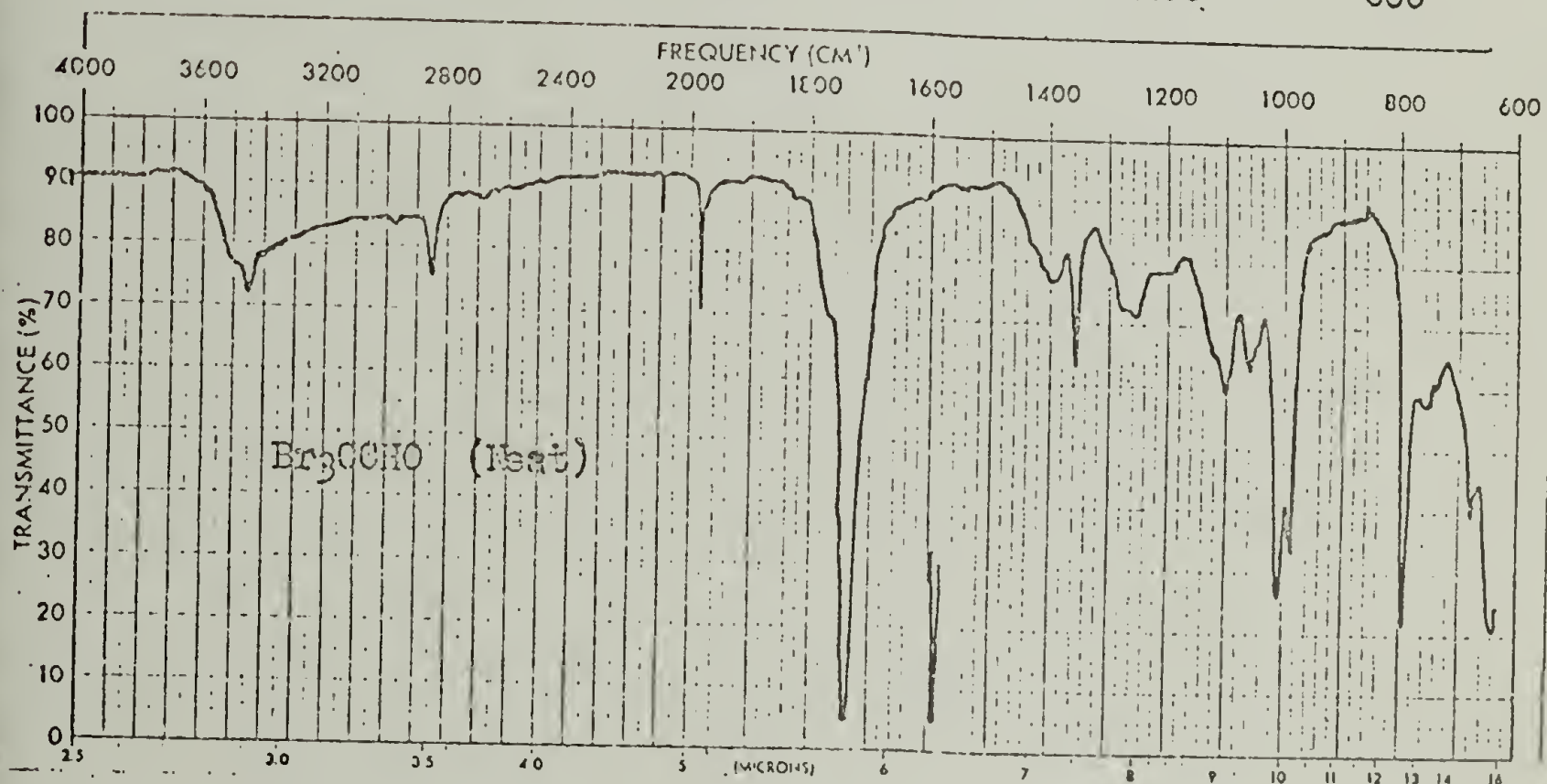
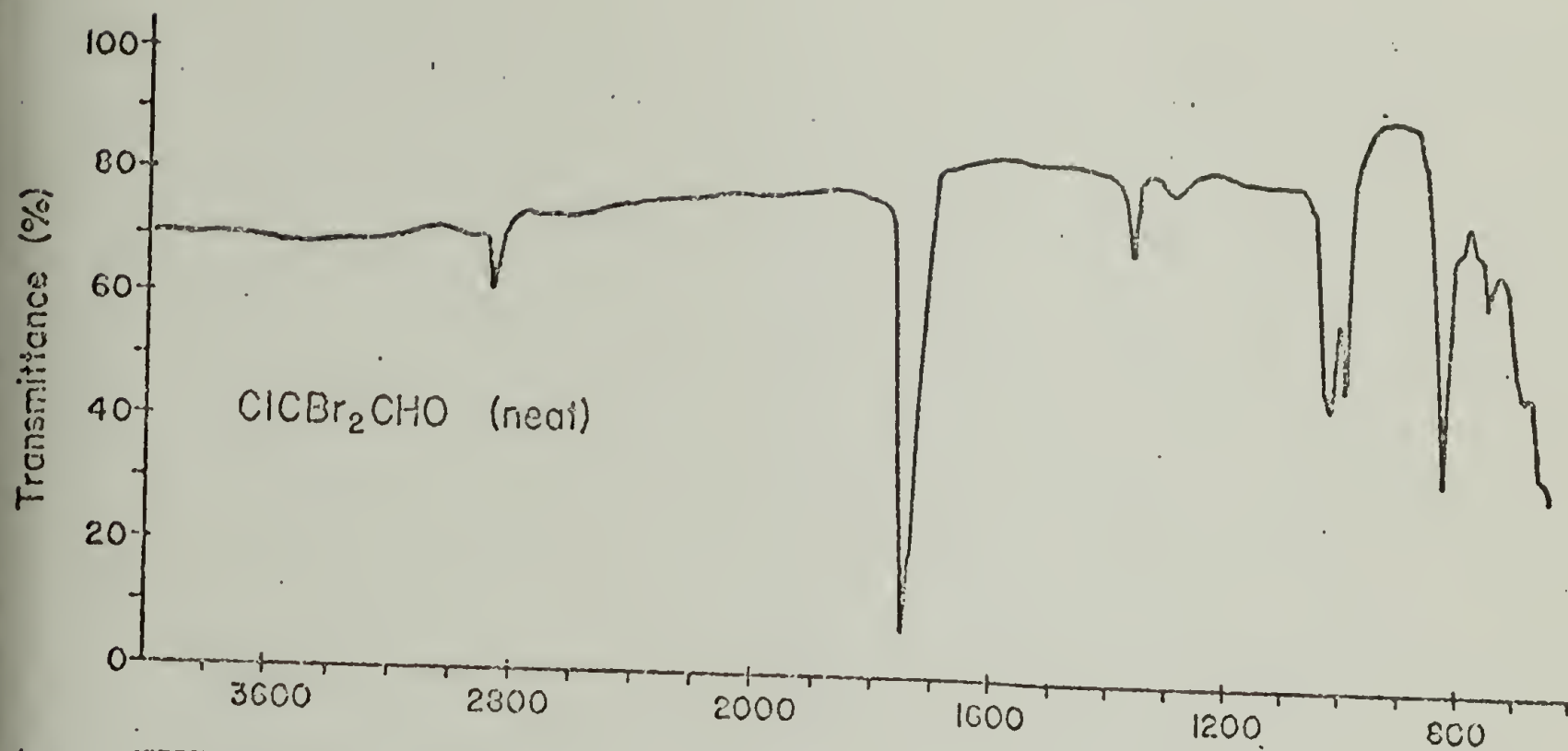
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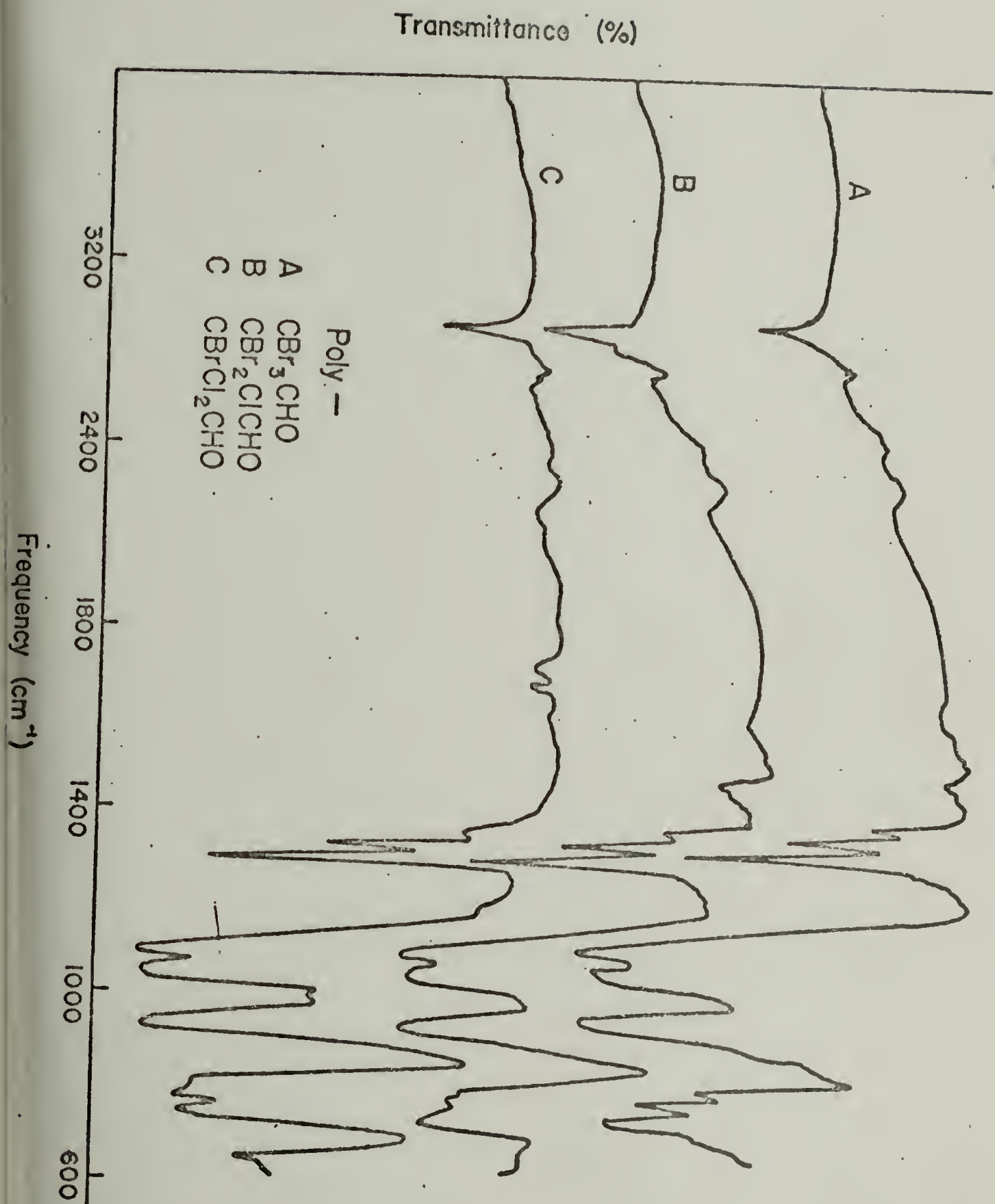
APPENDIX I - INFRARED SPECTRA



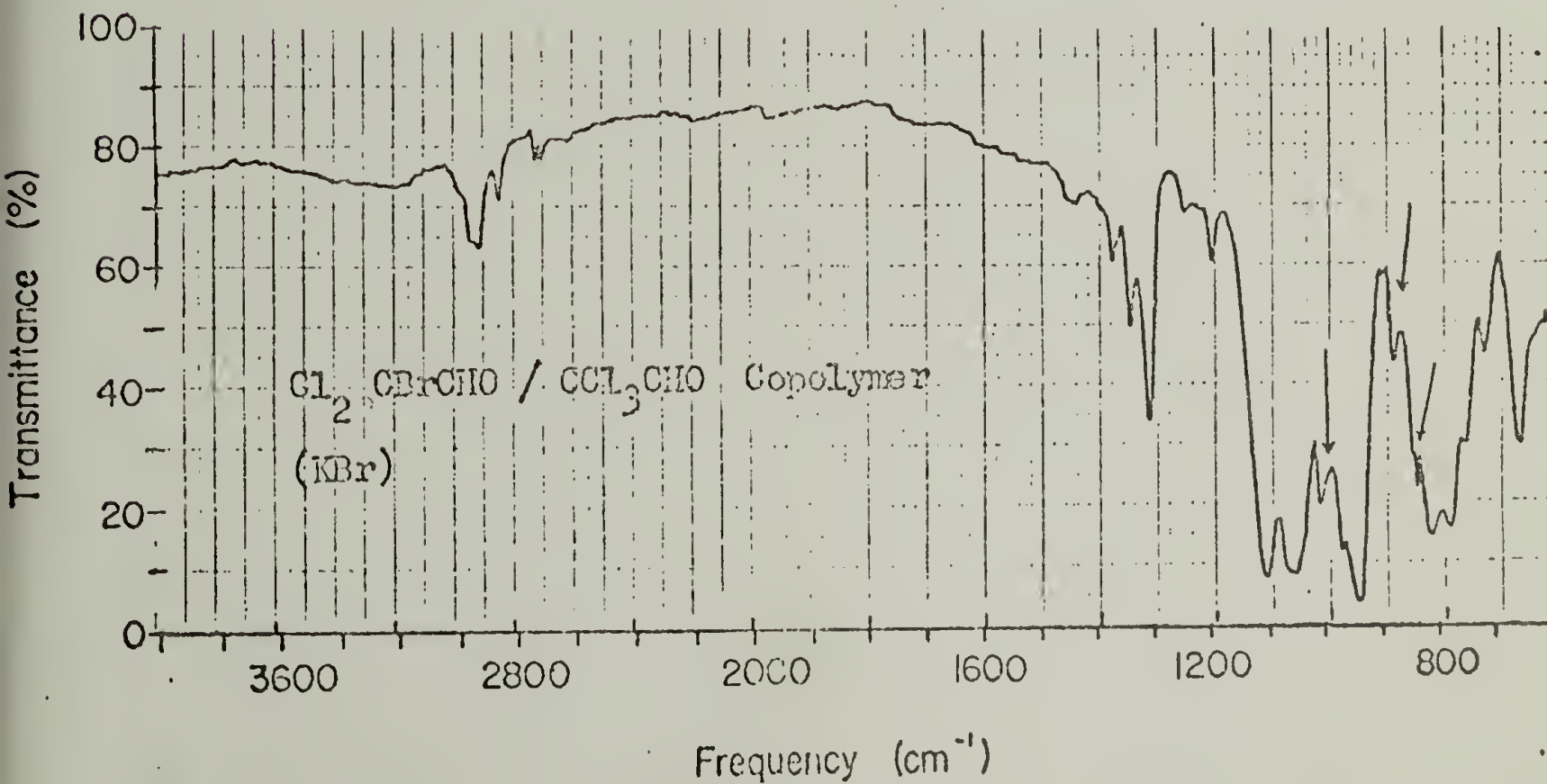
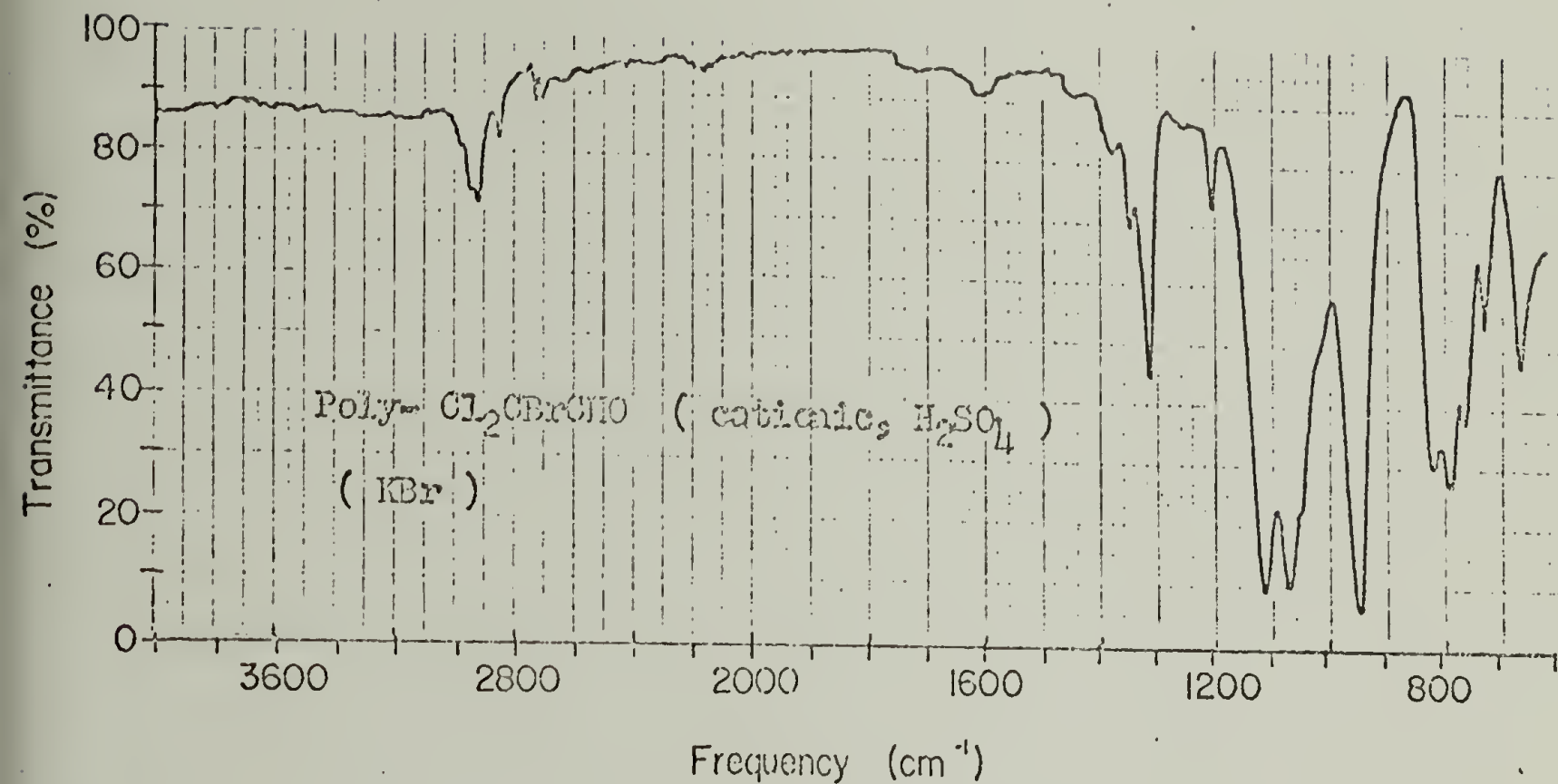


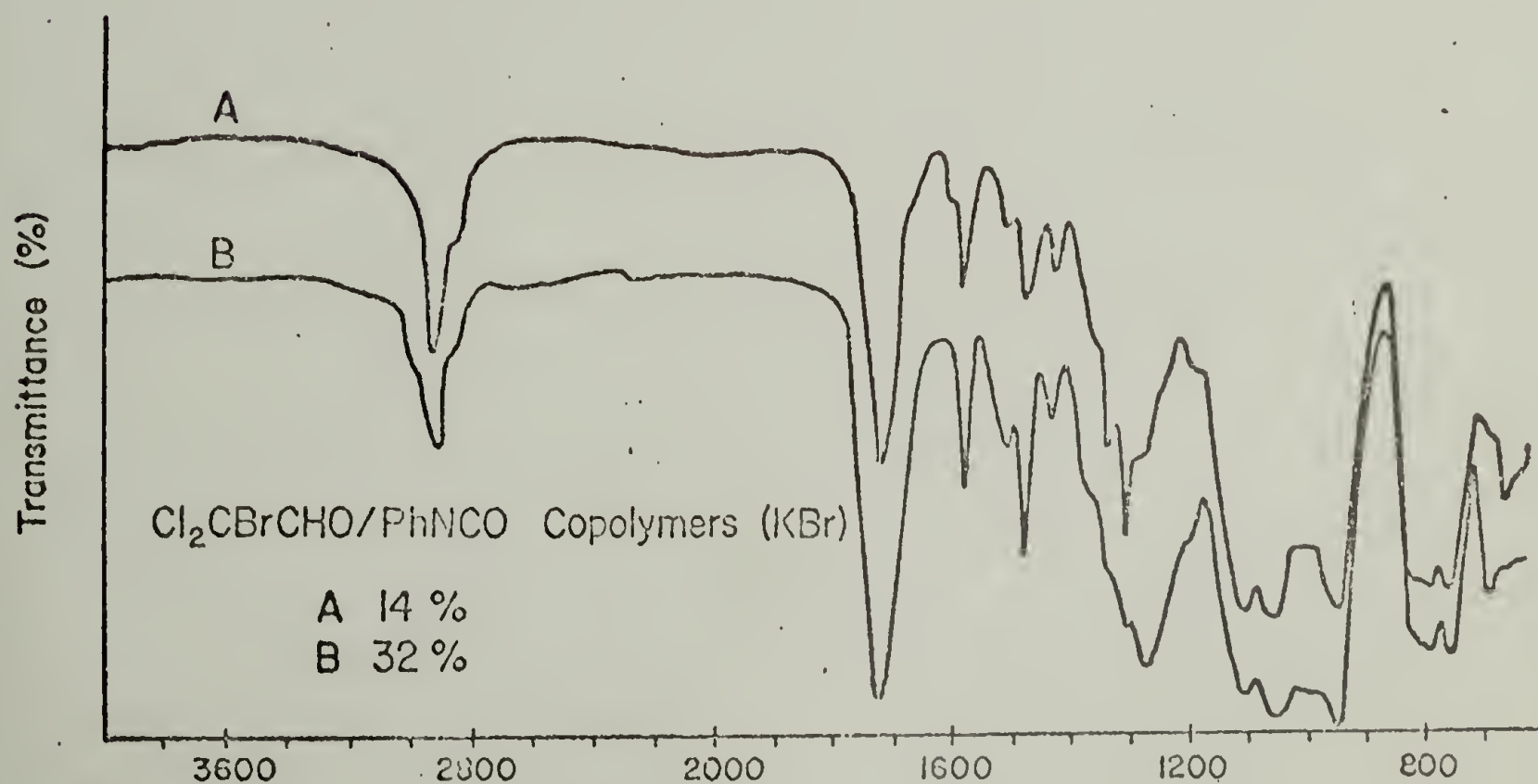
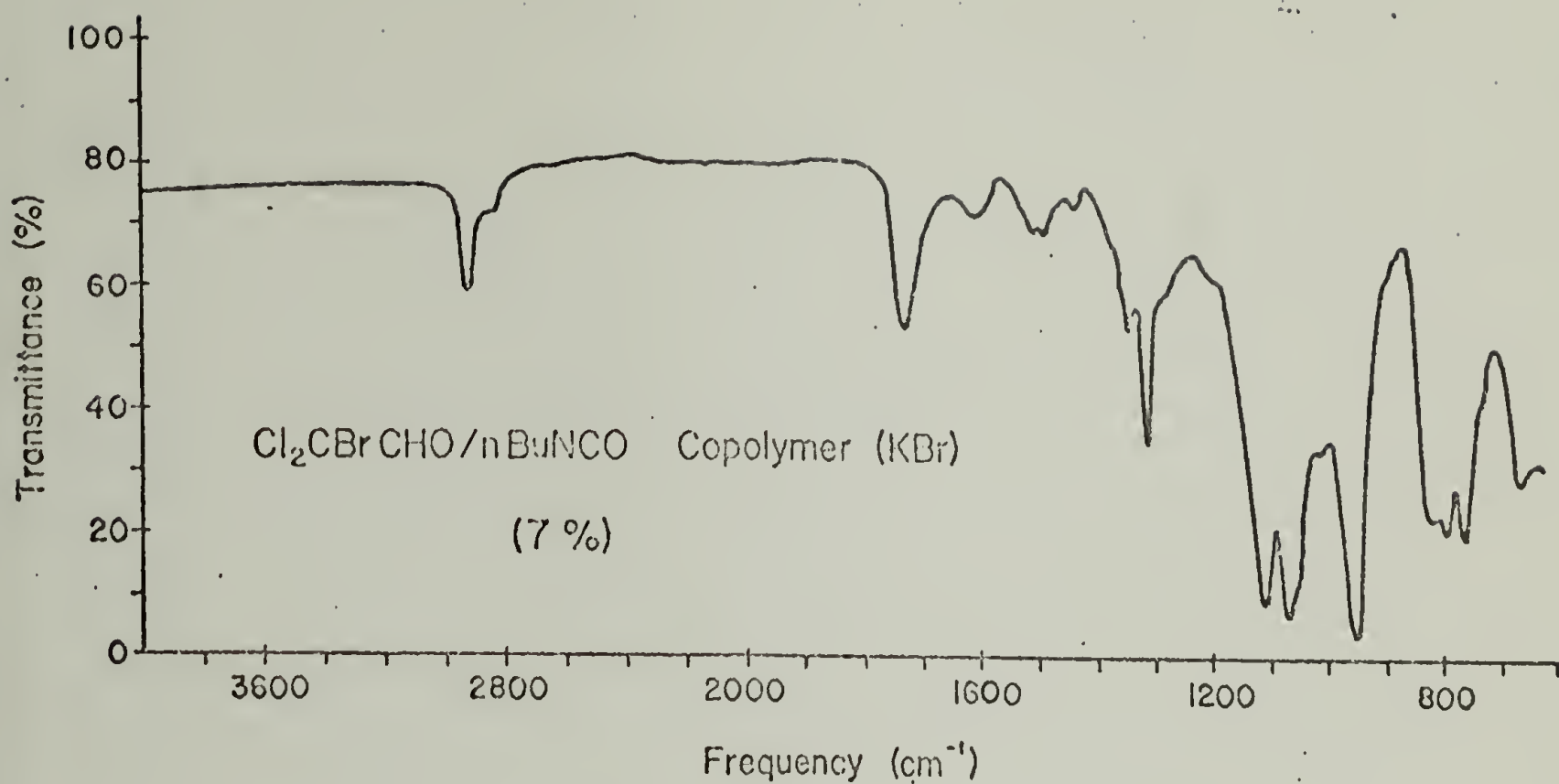


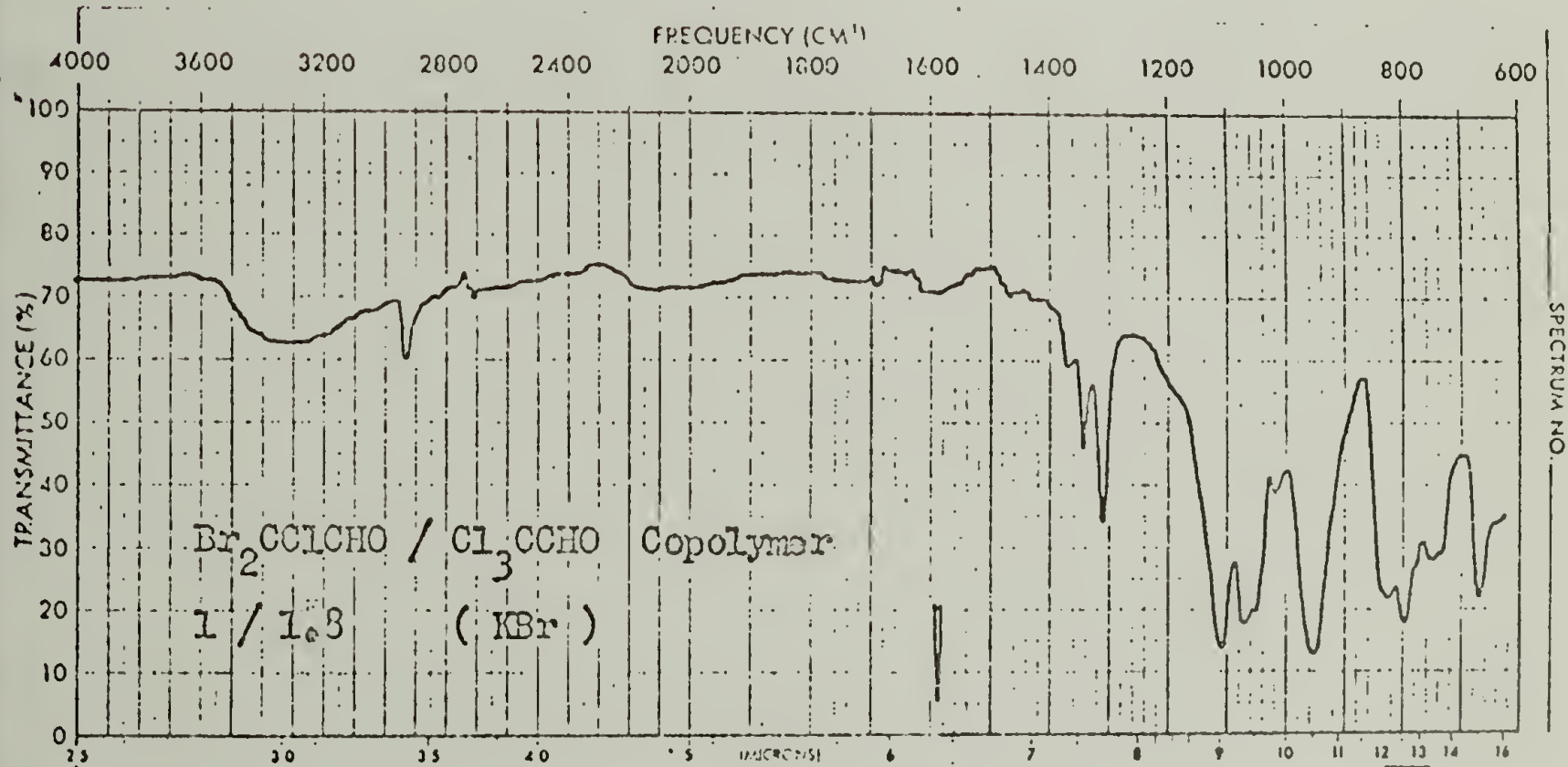
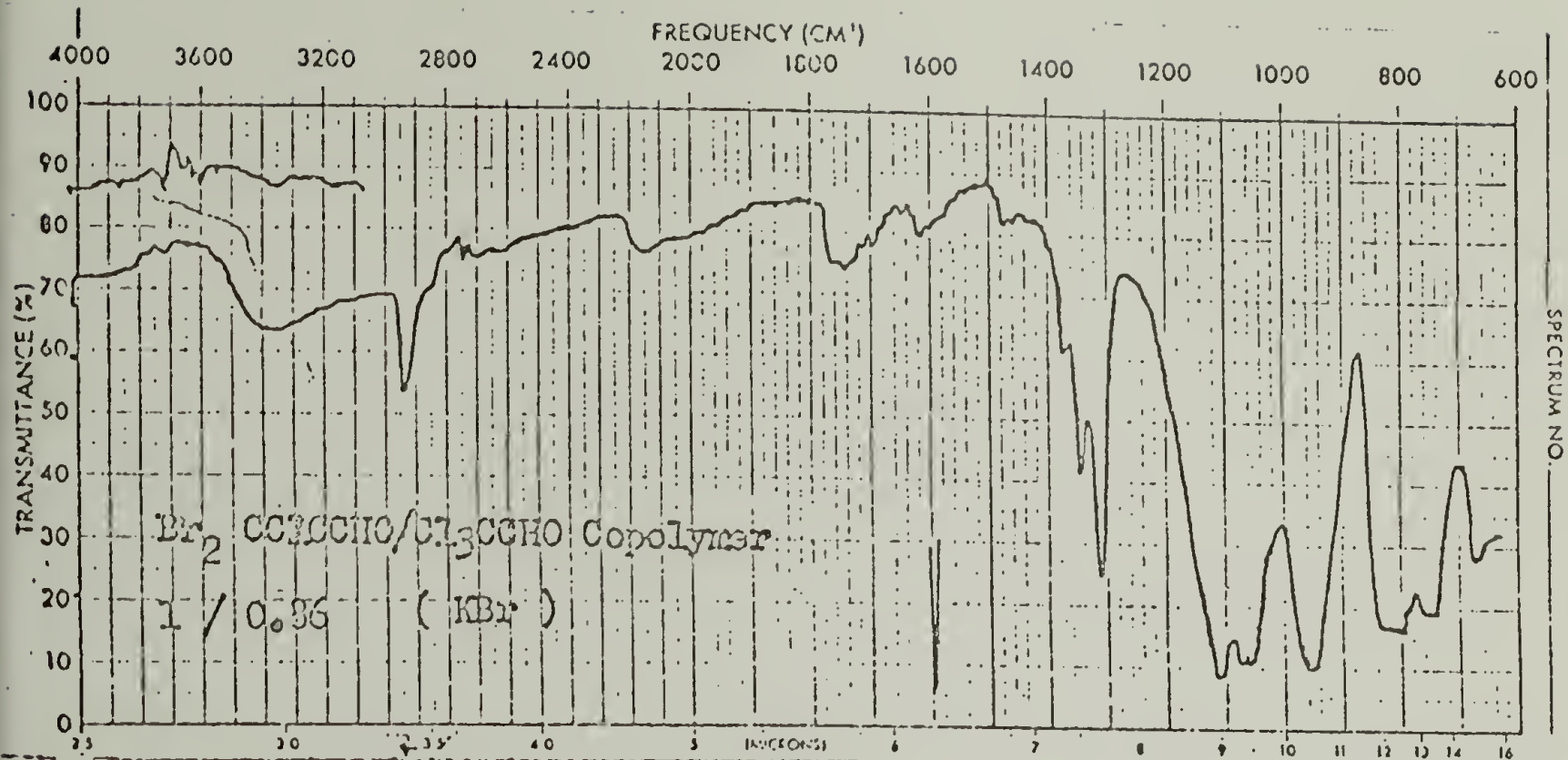
## INFRARED SPECTRA OF POLYPERHALOALDEHYDES (KBr PELLETS)



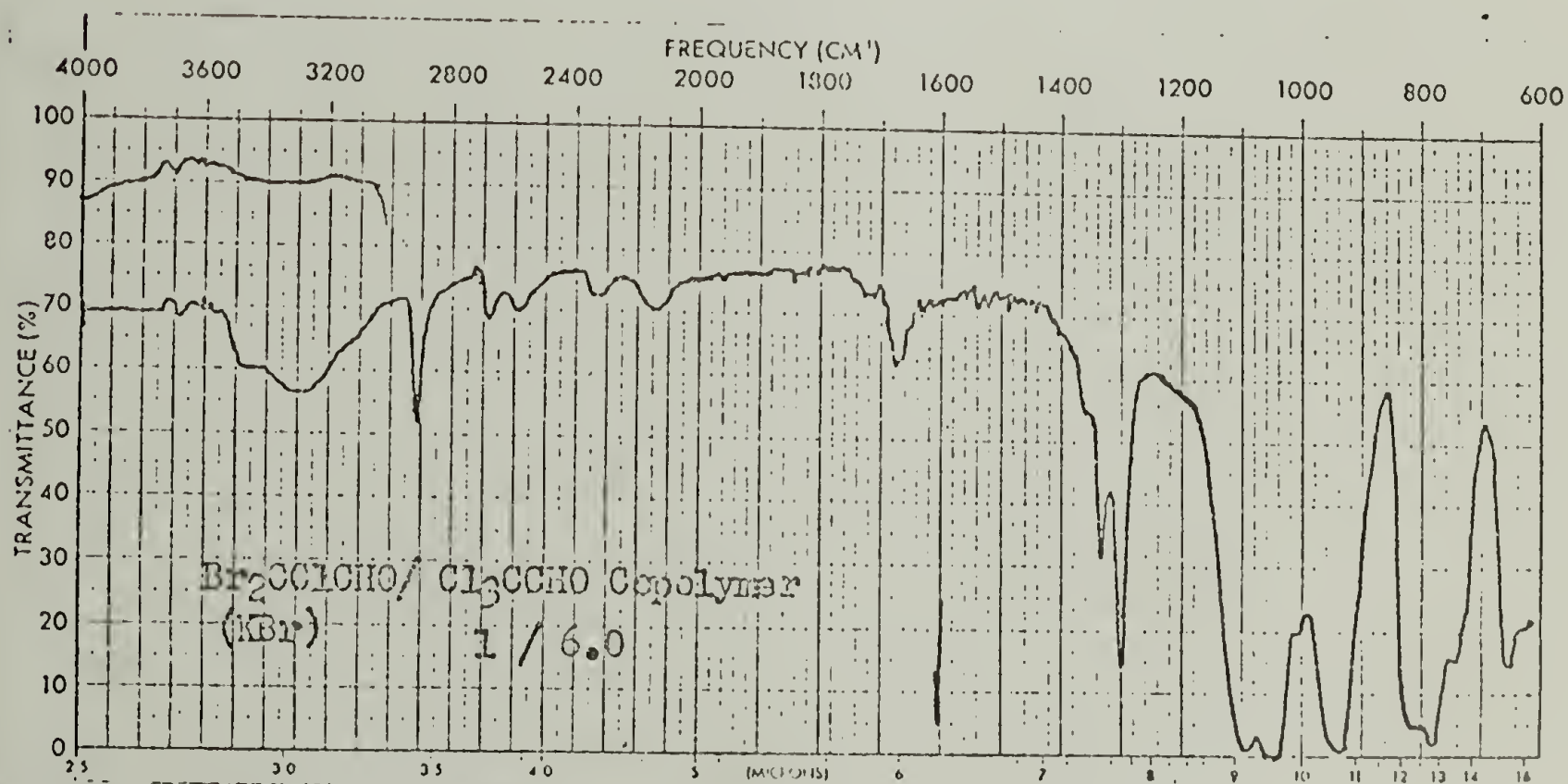
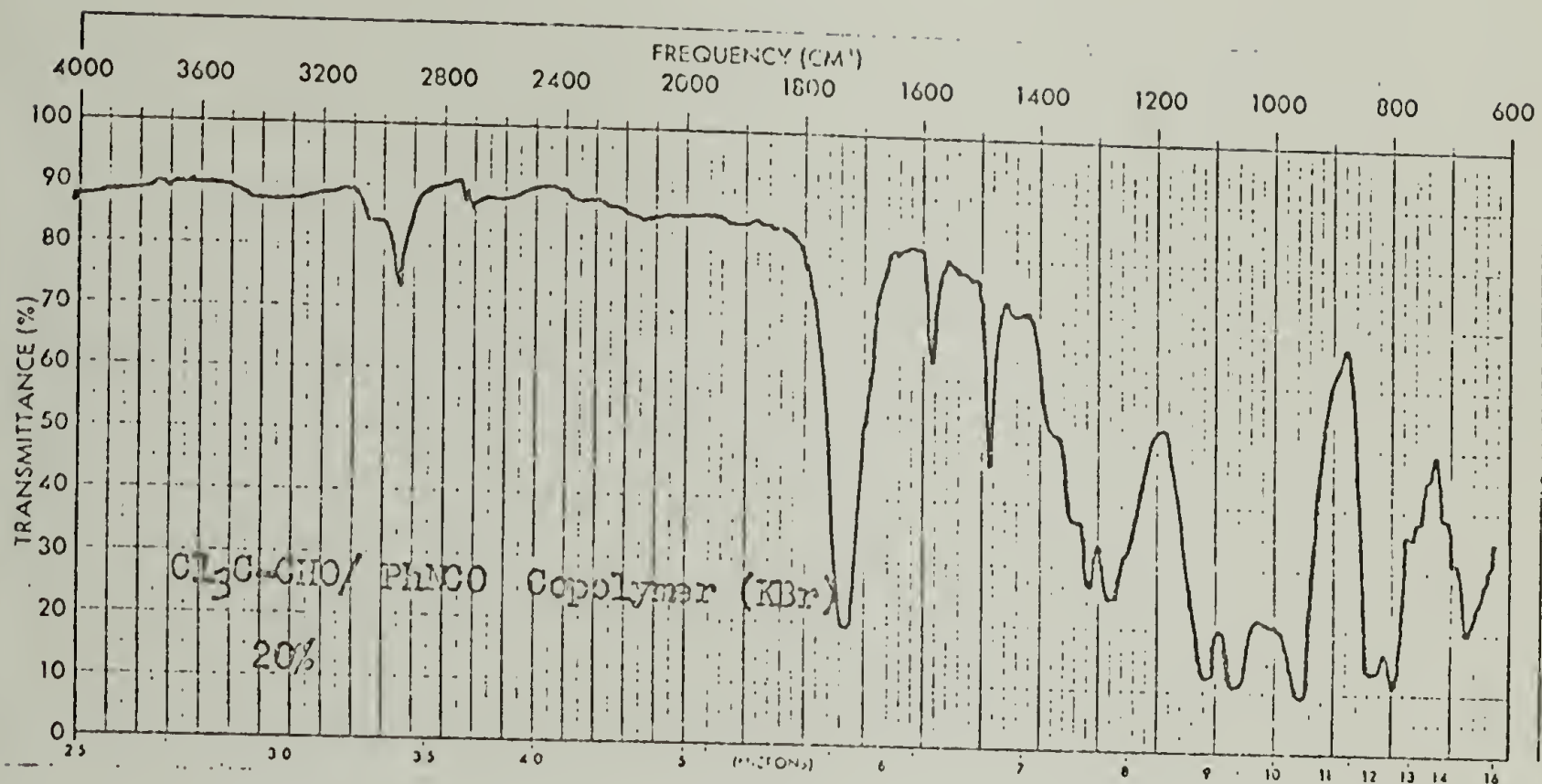
IR Spectrum (KBr) of Poly- $\text{Cl}_2\text{CBrCHO}$   
(cationic,  $\text{H}_2\text{SO}_4$ )

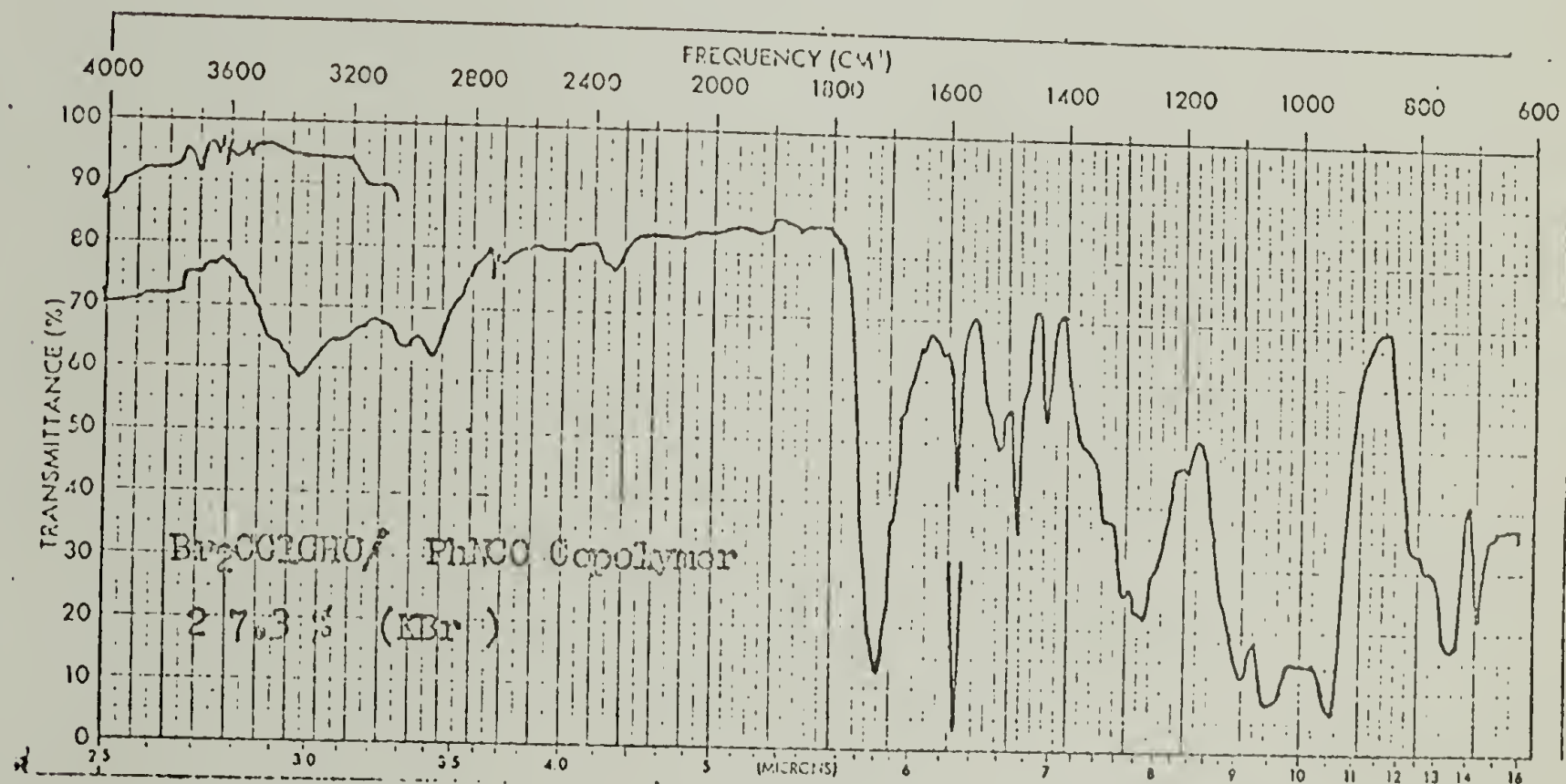
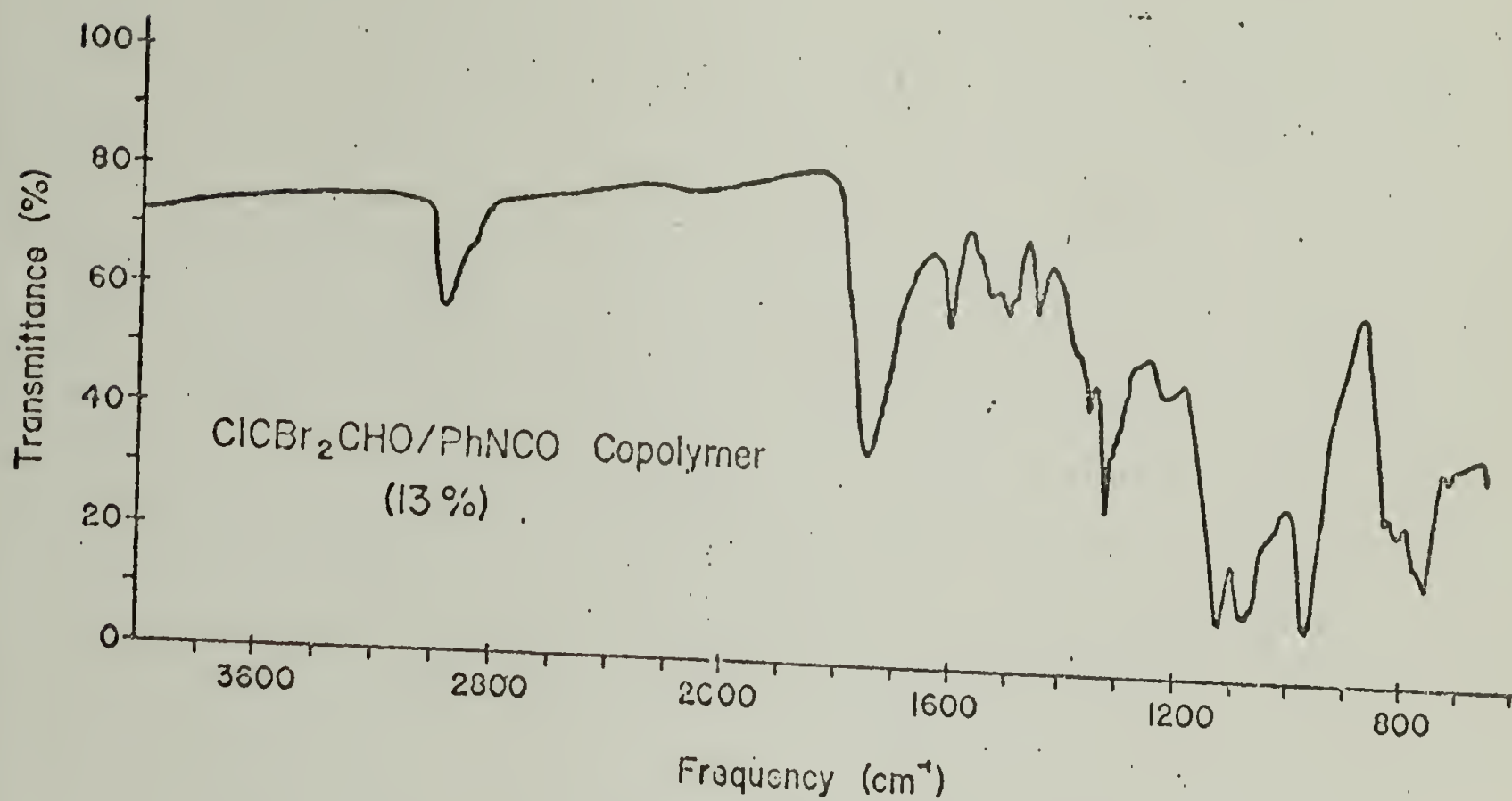


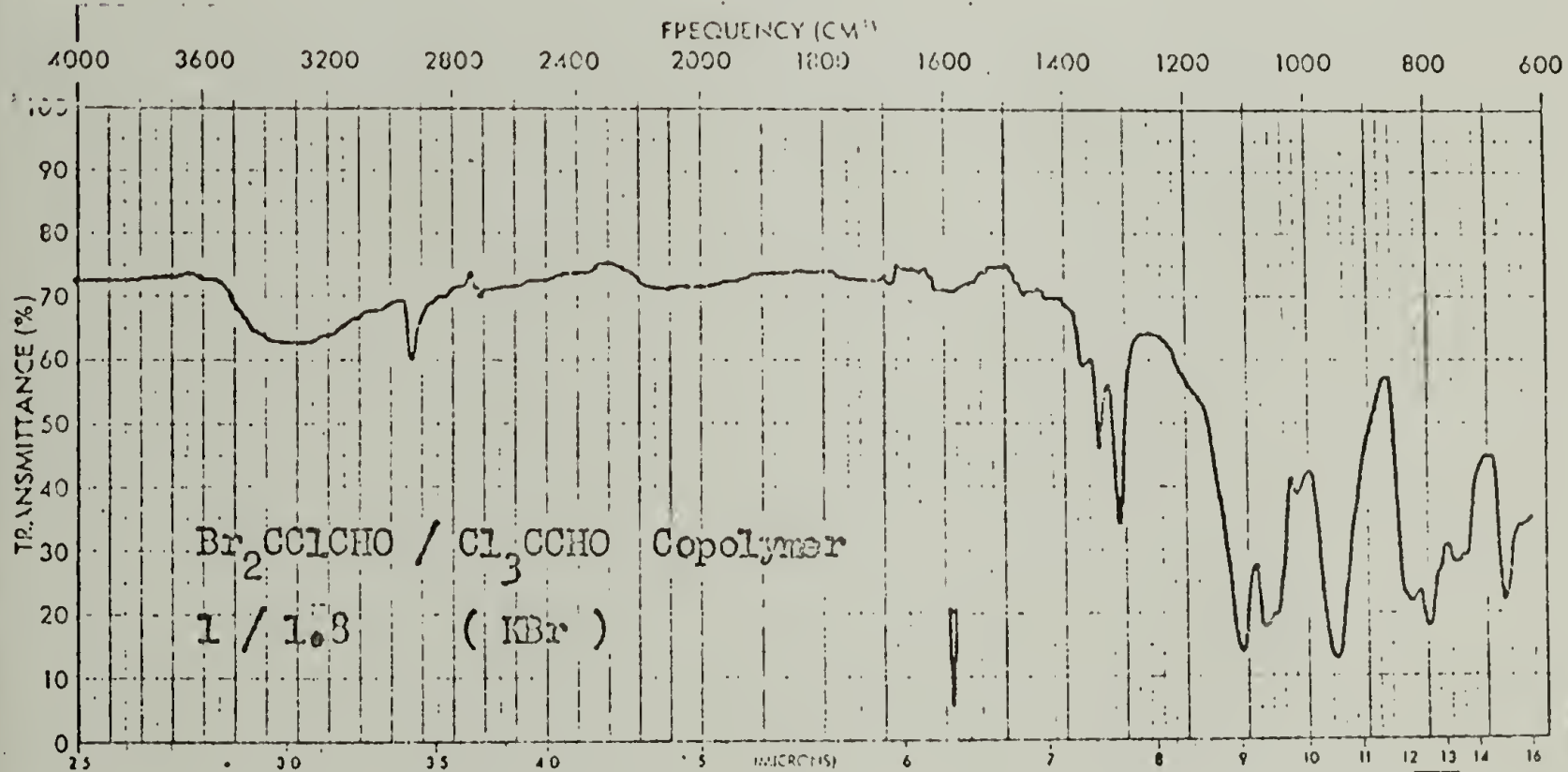
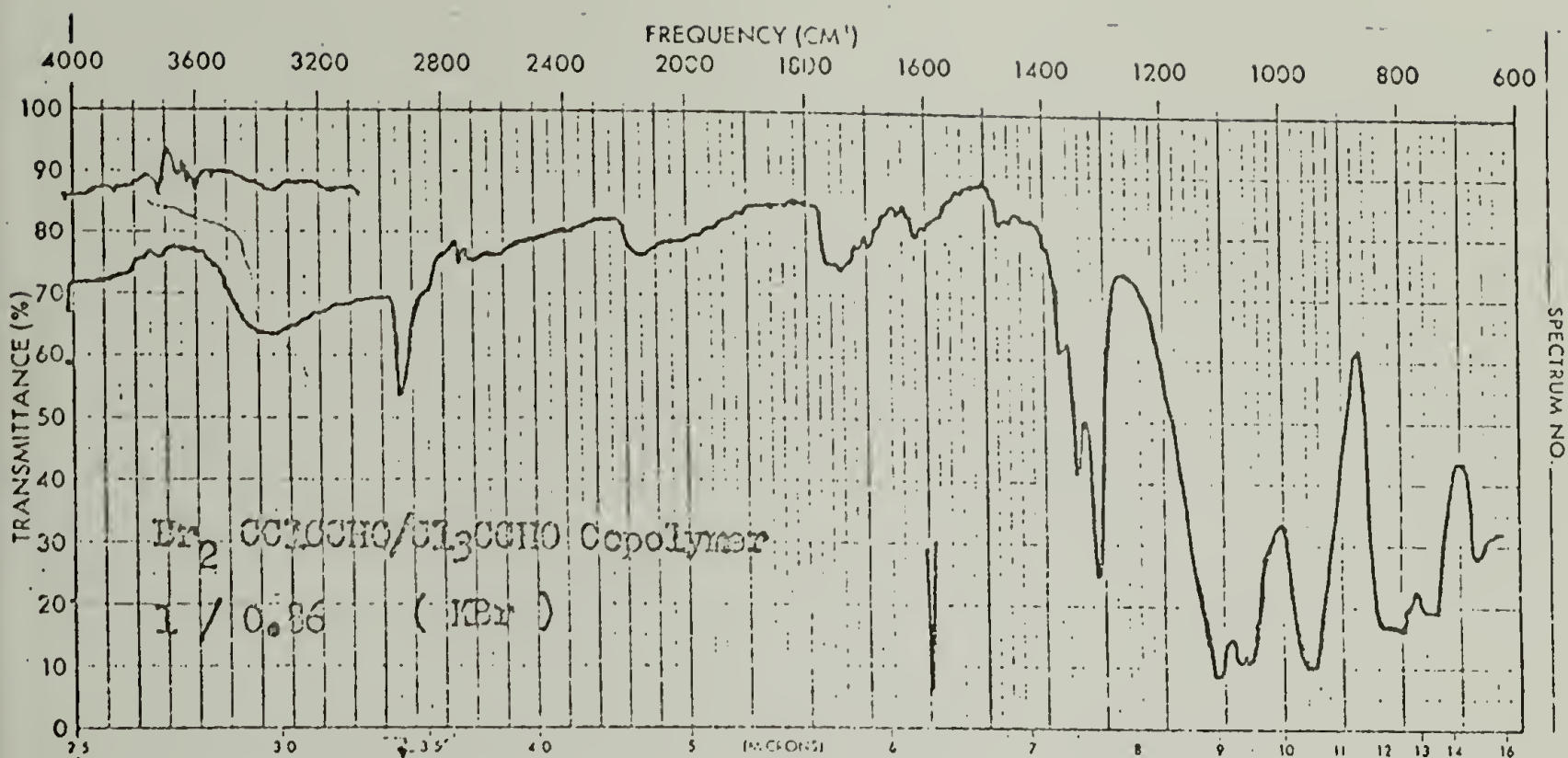




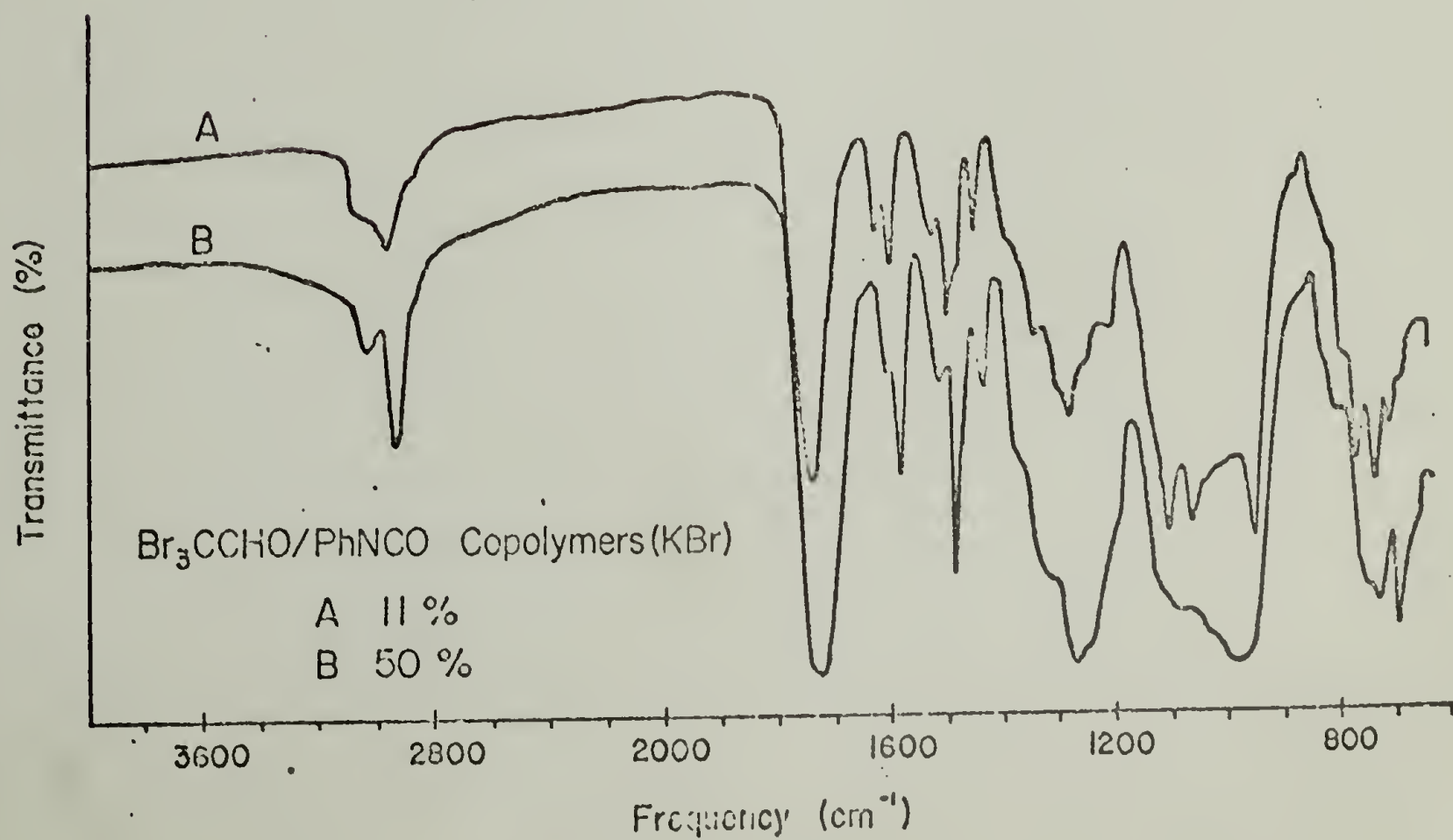
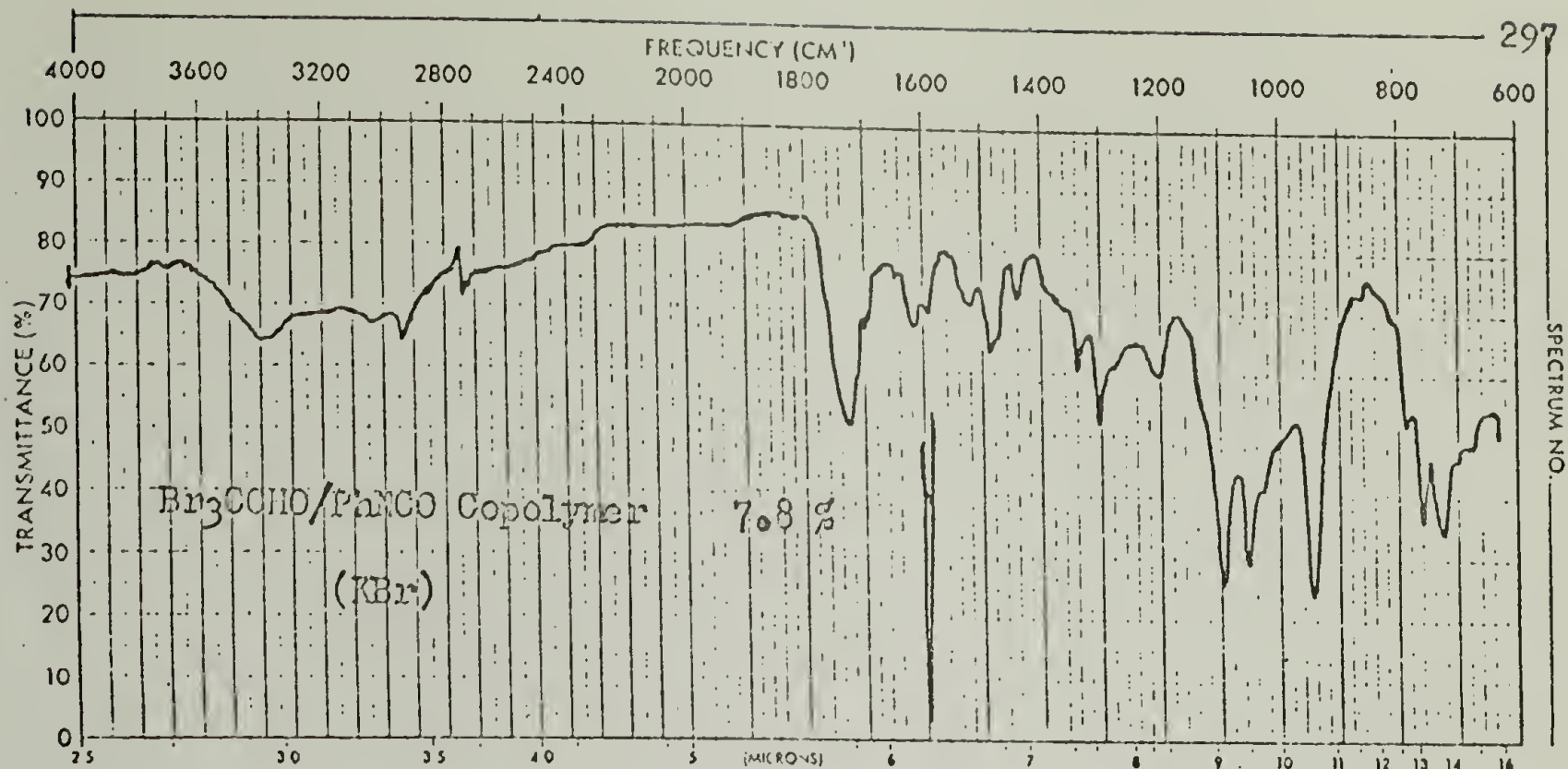




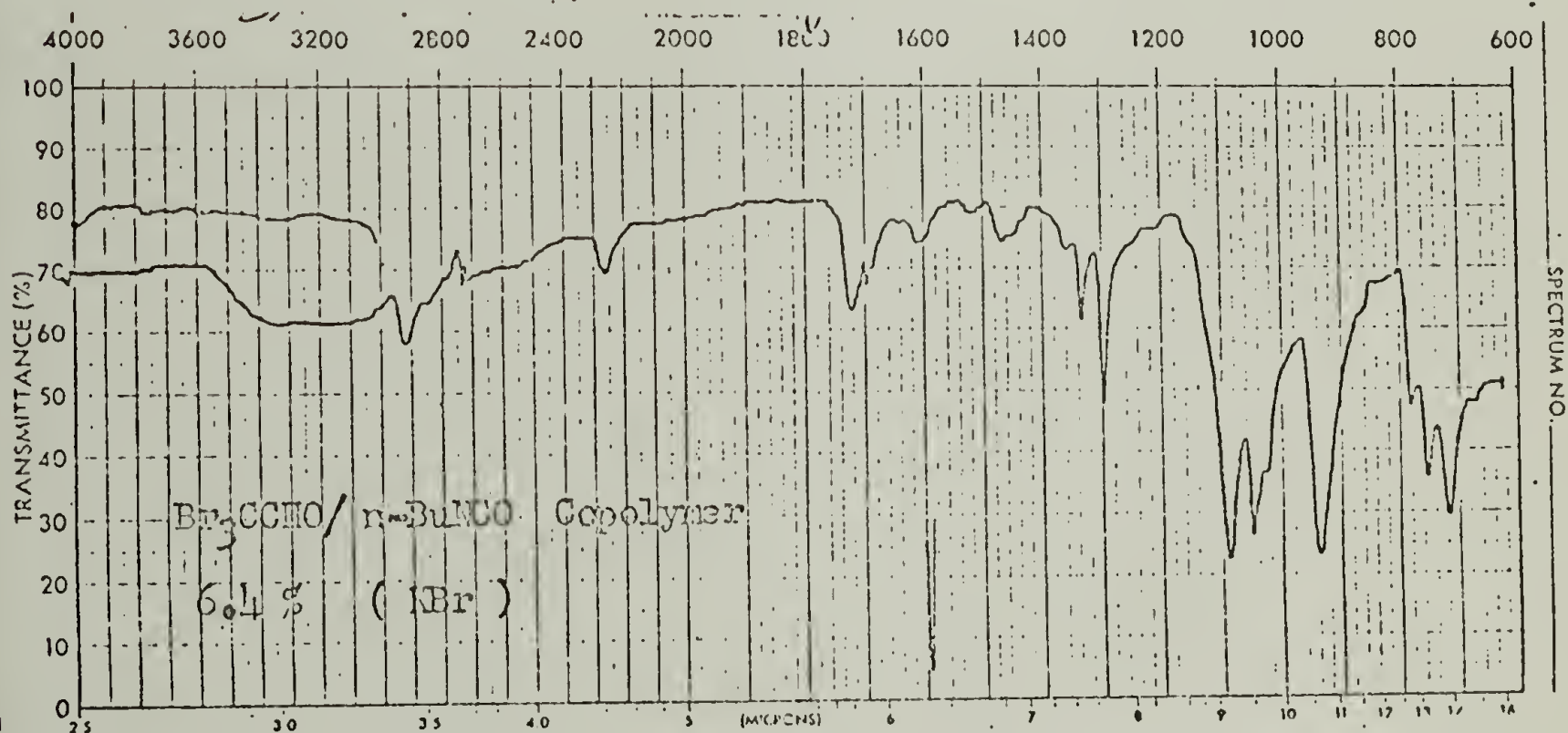
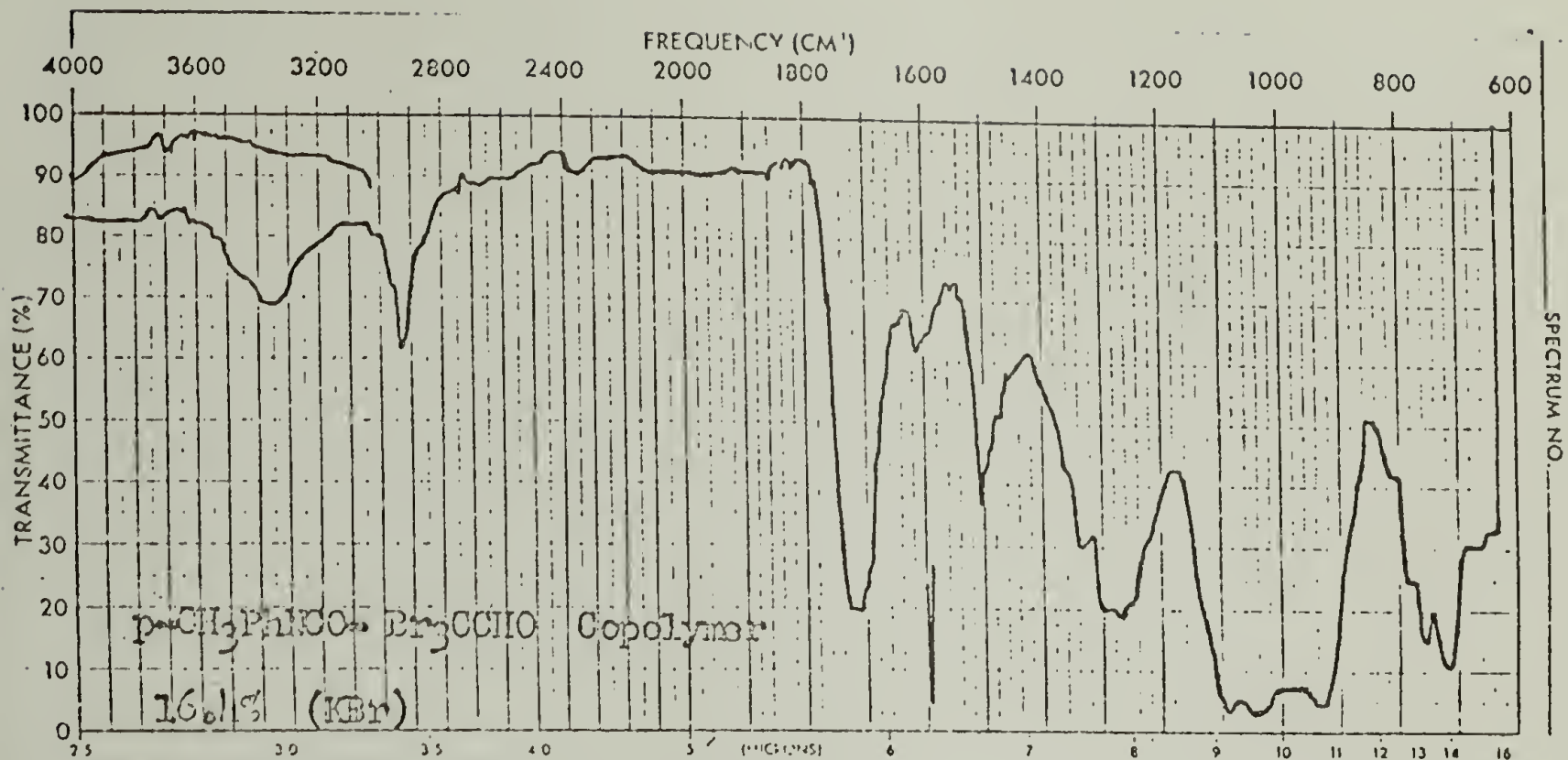


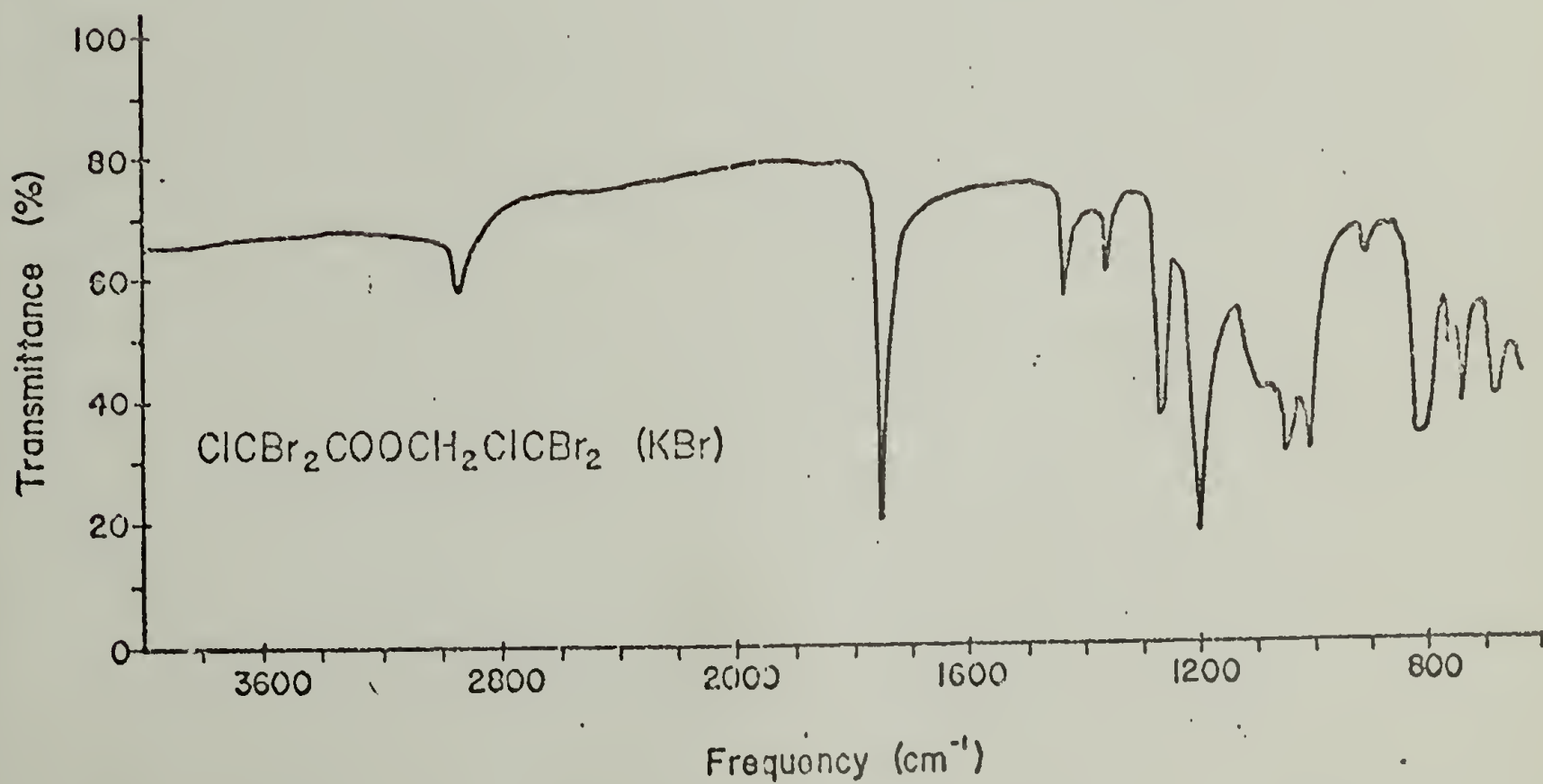
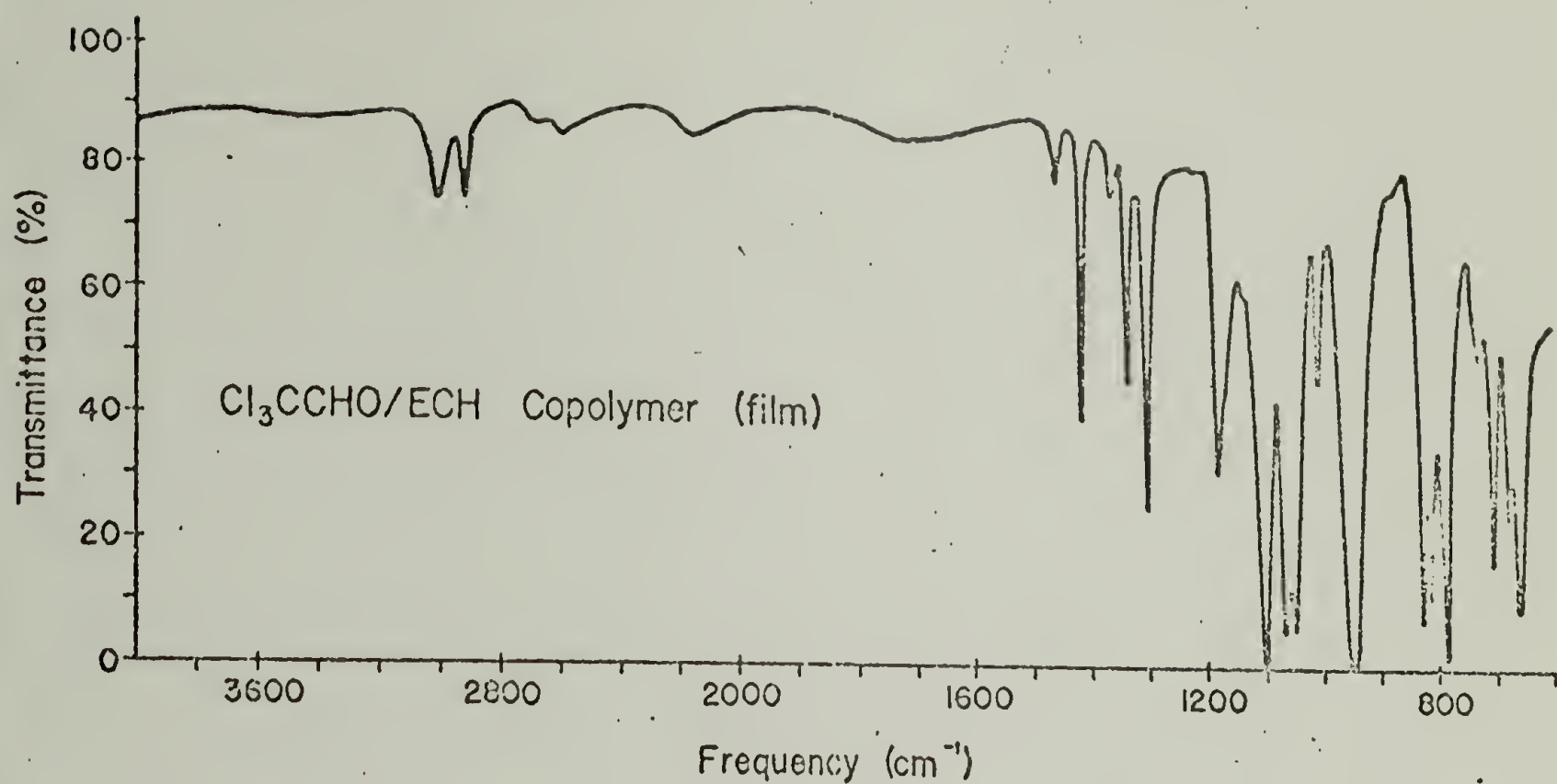








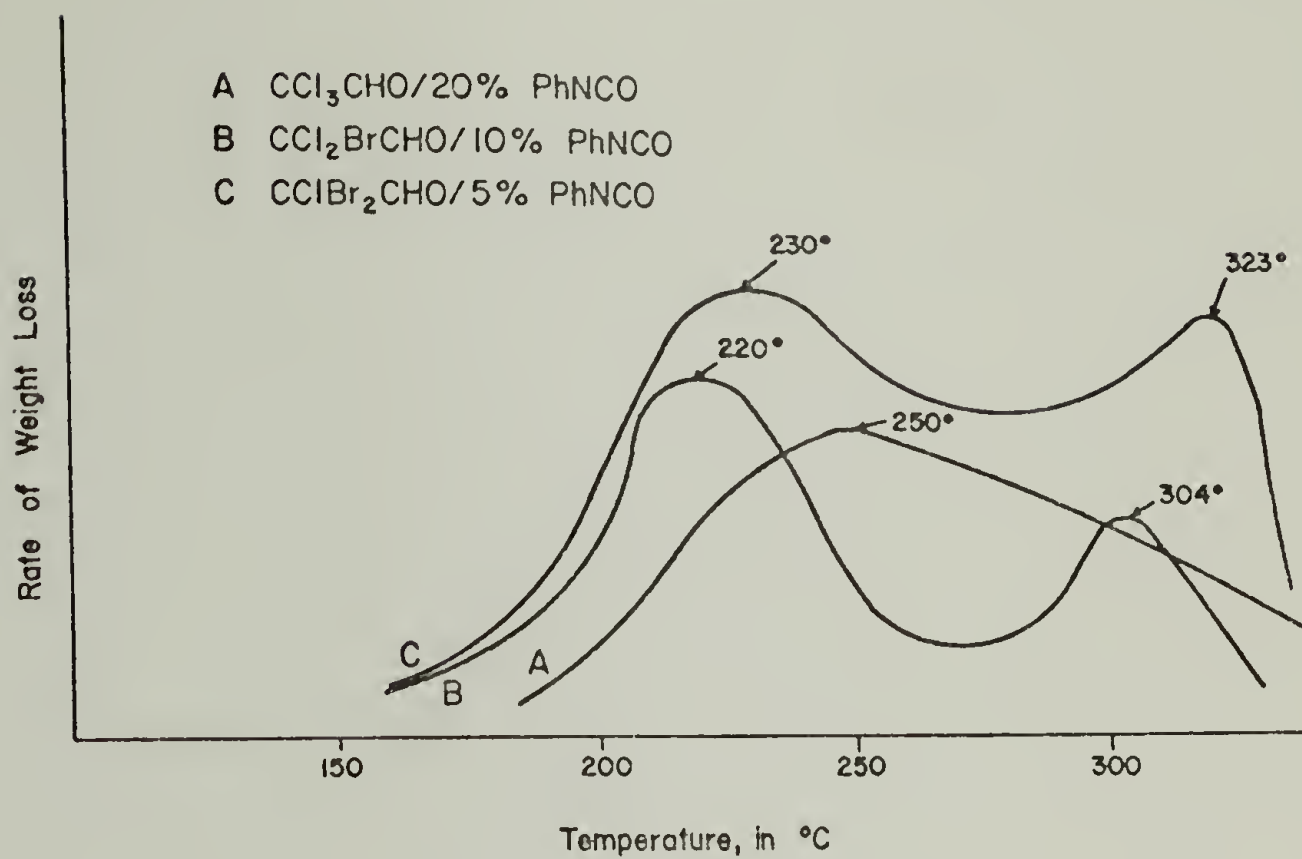




## APPENDIX II - THERMAL GRAVIMETRIC ANALYSIS

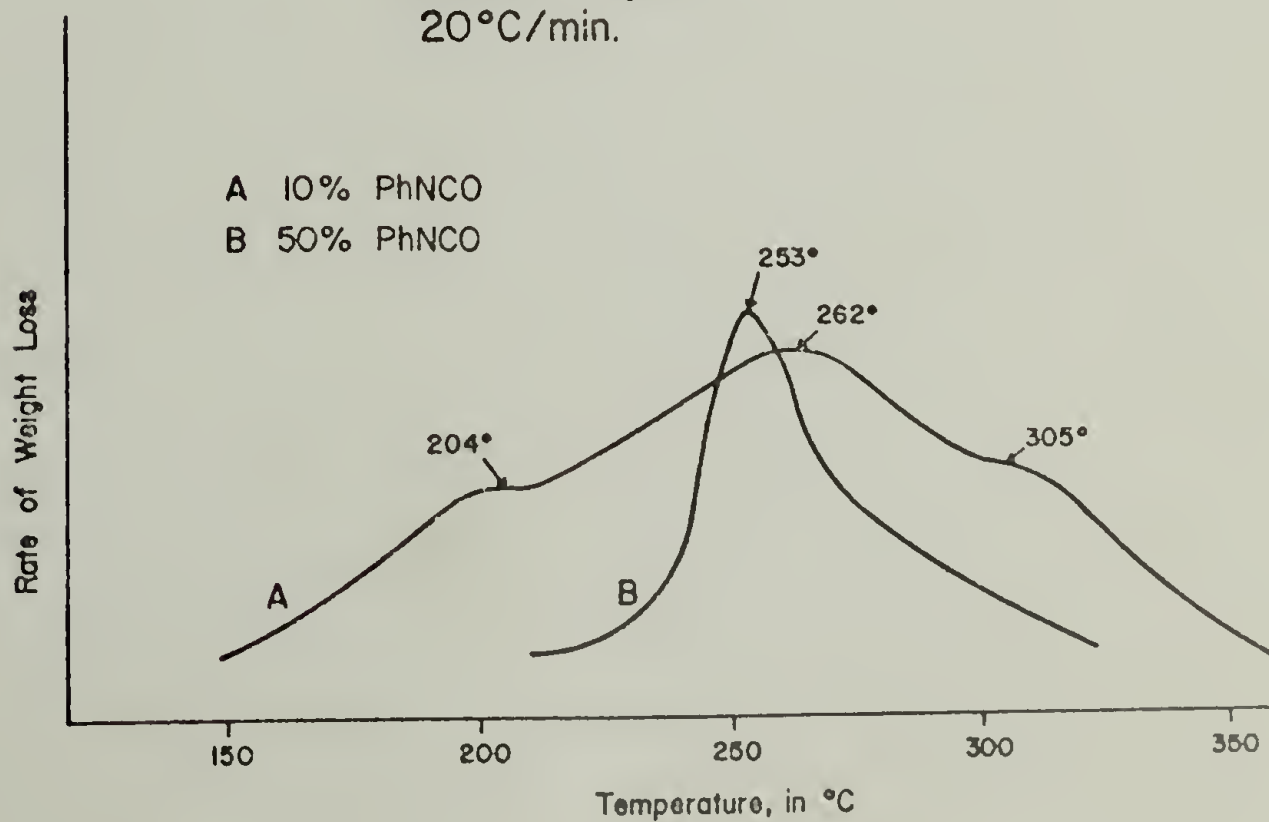
## DTG CURVES OF HALOALDEHYDE — COPOLYMERS

Initiator: Pyridine (2 mole %)  
20°C/min.



## DTG CURVES OF BROMAL — PHENYLISOCYANATE COPOLYMERS

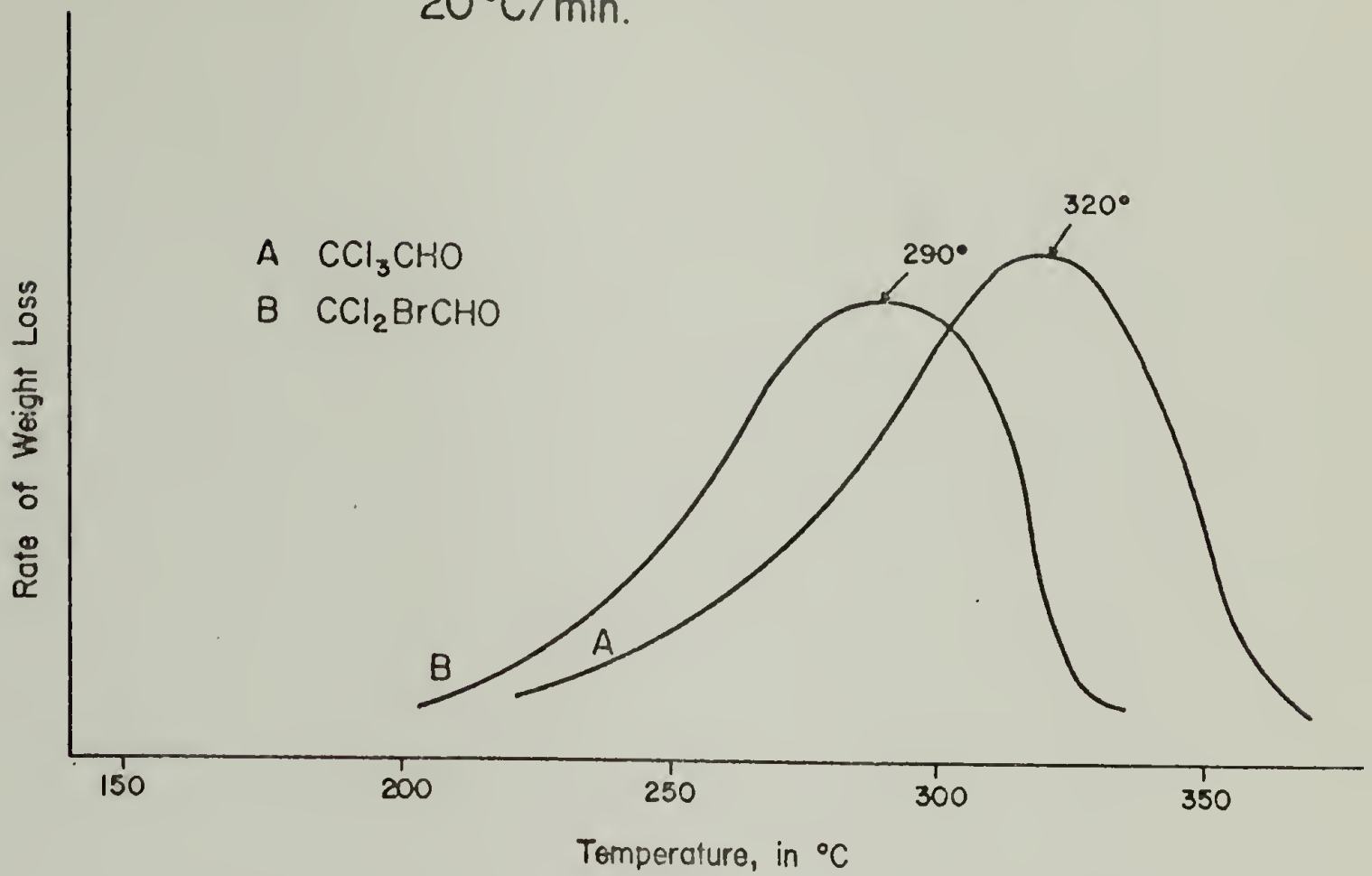
Initiator: Pyridine  
20°C/min.





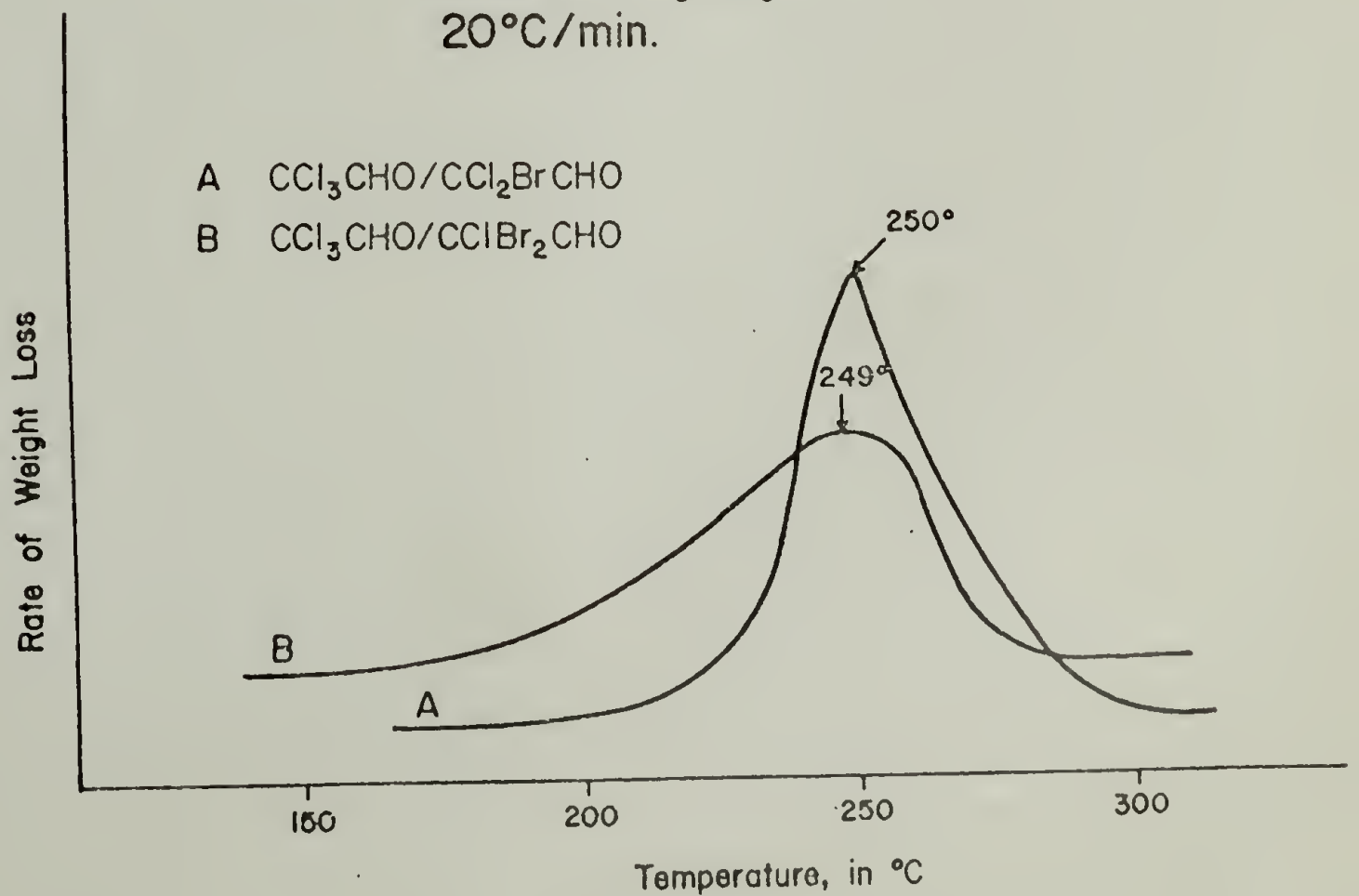
## DTG CURVES OF HALOALDEHYDE POLYMERS

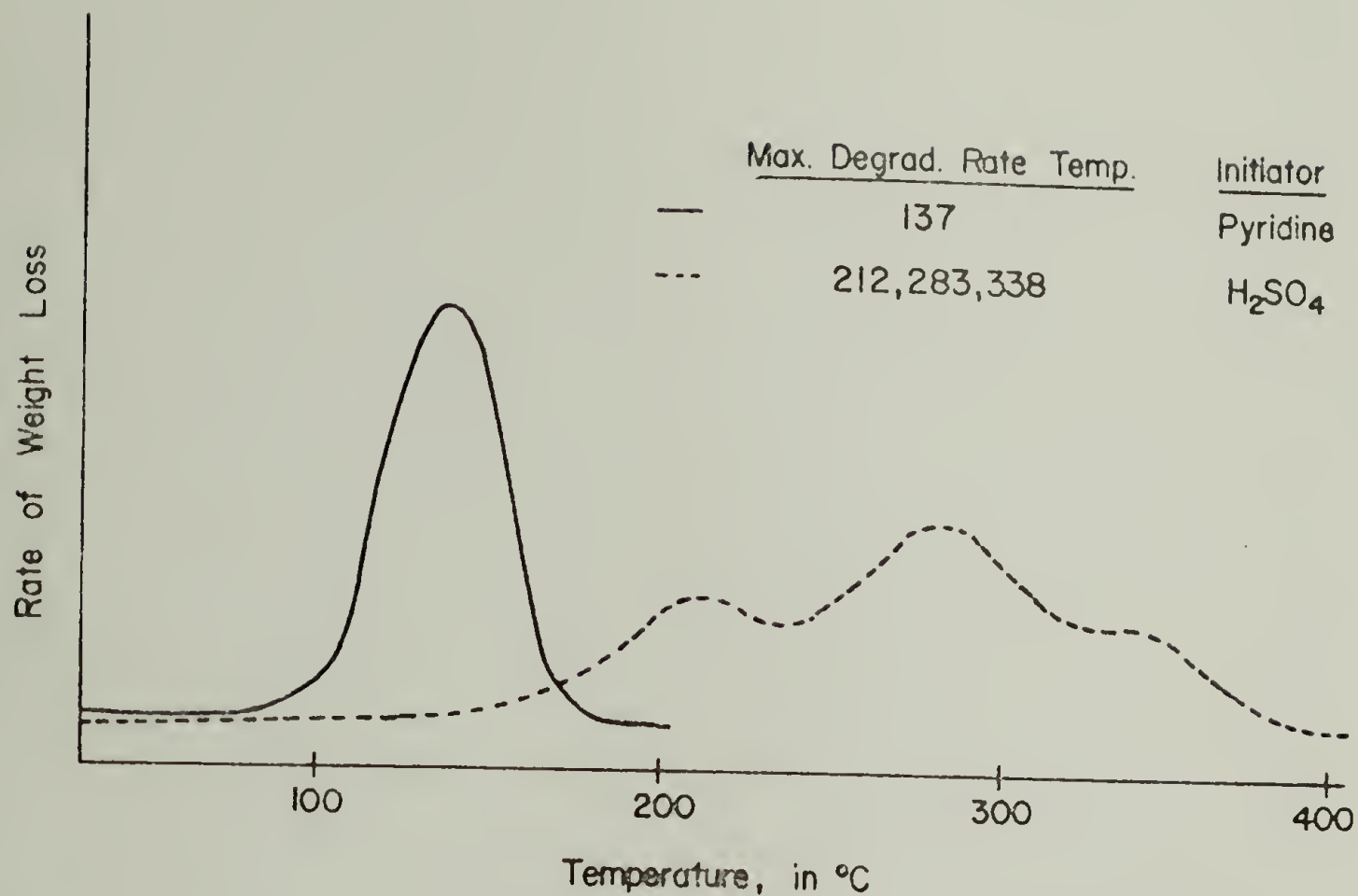
Initiator:  $\text{CF}_3\text{SO}_3\text{H}$   
 $20^\circ\text{C}/\text{min.}$



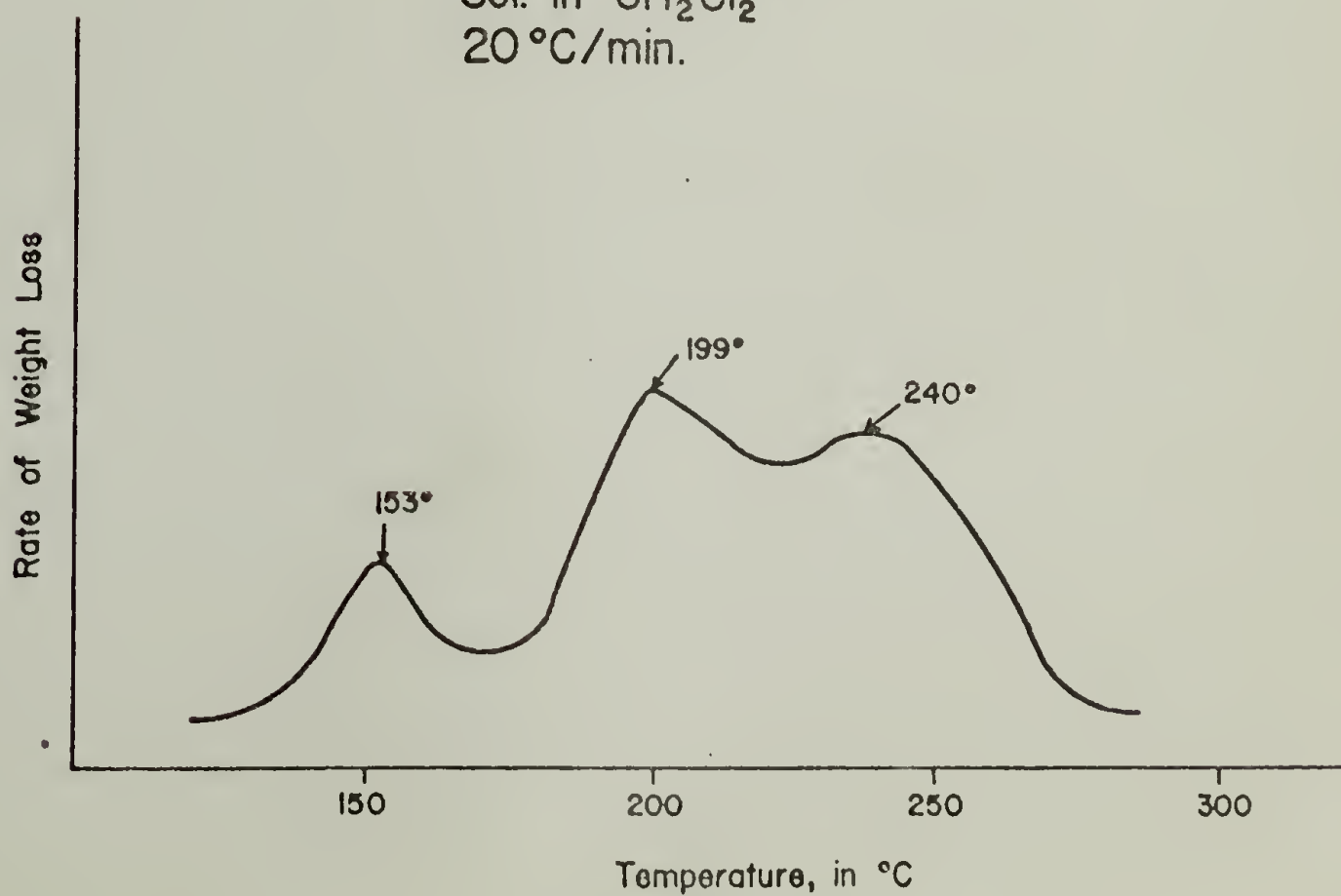
## DTG CURVES OF CHLORAL COPOLYMERS

Initiator:  $\text{CF}_3\text{SO}_3\text{H}$   
 $20^\circ\text{C}/\text{min.}$



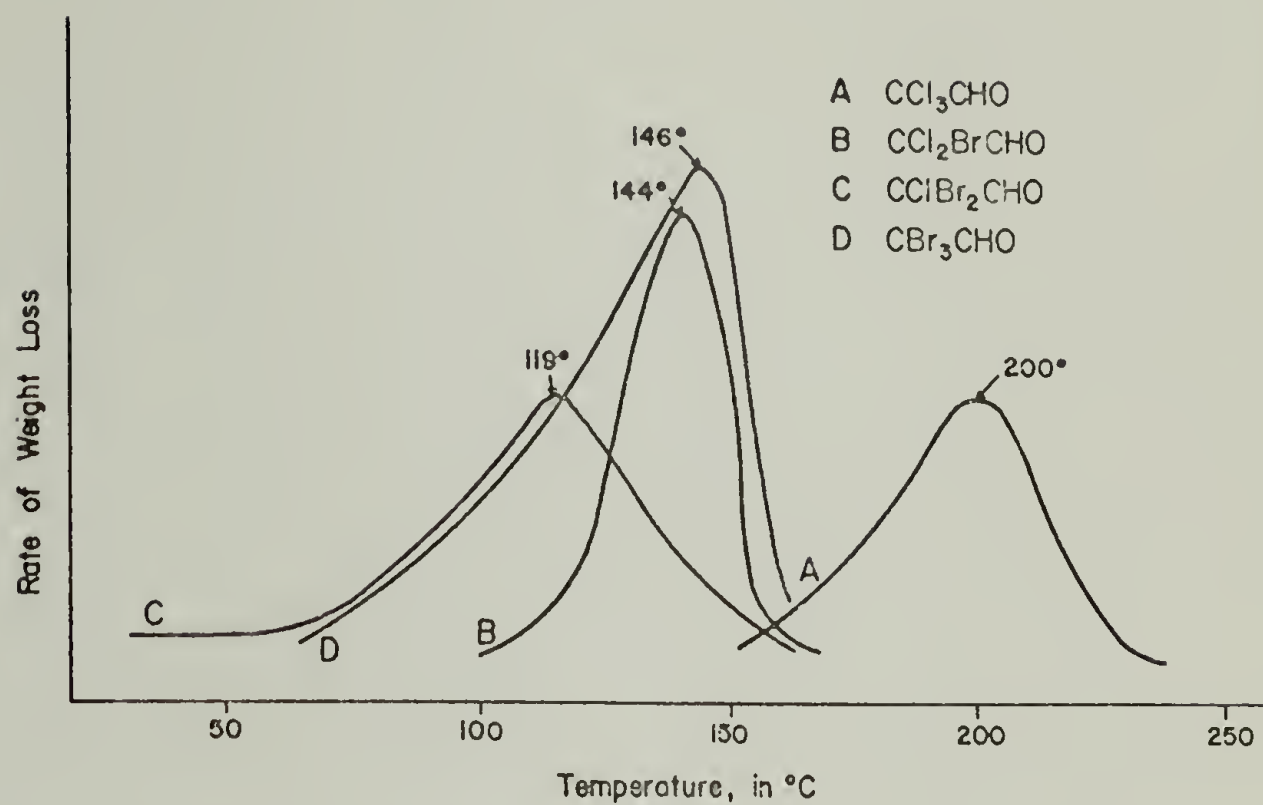
DTG Curve of Poly- $\text{Cl}_2\text{CBrCHO}$ DTG CURVE OF POLY- $\text{CCl}_2\text{BrCHO}$ 

Initiator:  $\text{H}_2\text{SO}_4$   
Sol. in  $\text{CH}_2\text{Cl}_2$   
 $20^{\circ}\text{C}/\text{min.}$



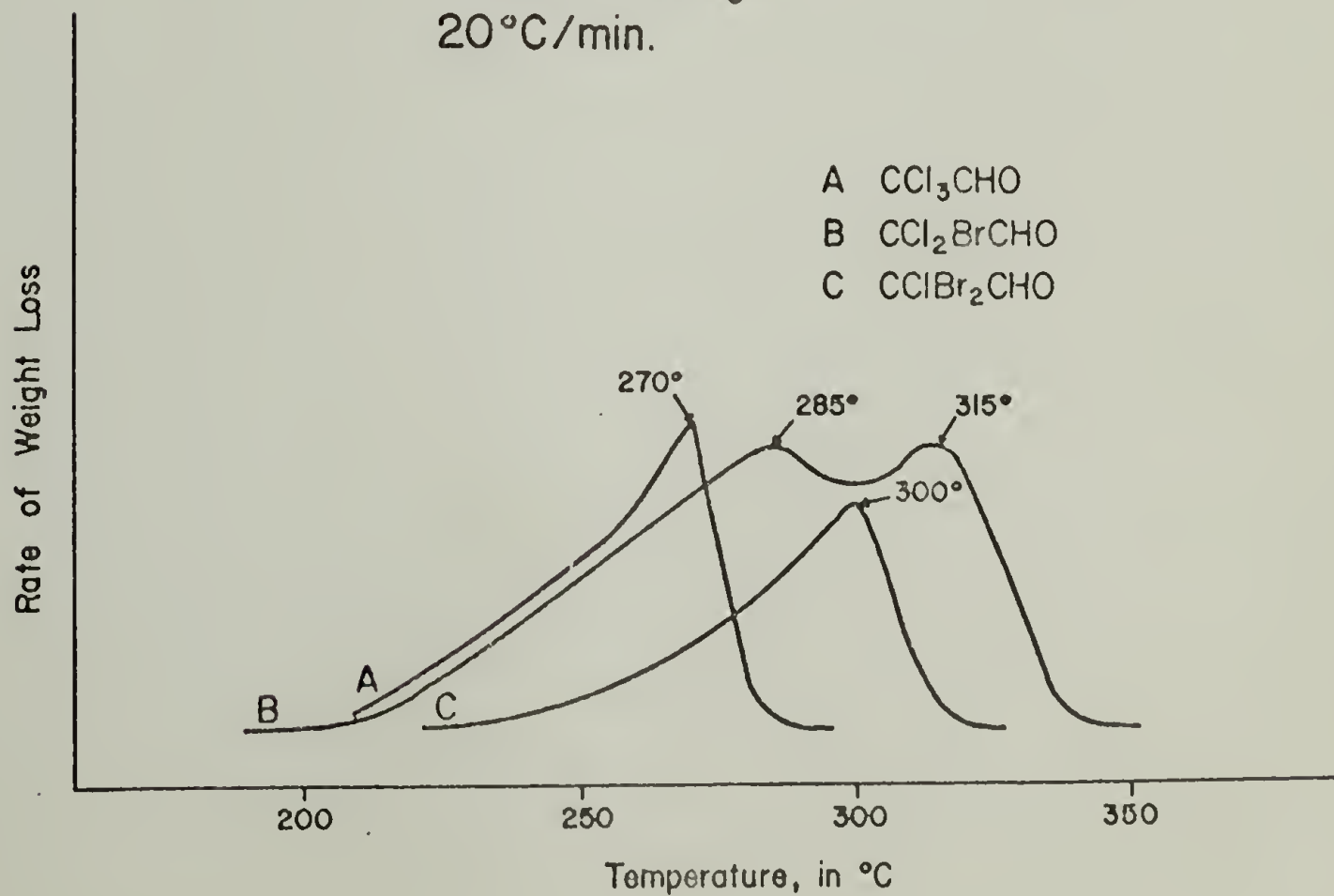
## DTG CURVES OF HALOALDEHYDE POLYMERS

Initiator: Pyridine  
20°C/min.



## DTG CURVES OF HALOALDEHYDE POLYMERS

Initiator:  $\text{SbCl}_5$   
20°C/min.



### APPENDIX III - NMR SPECTRA AND RATE STUDIES

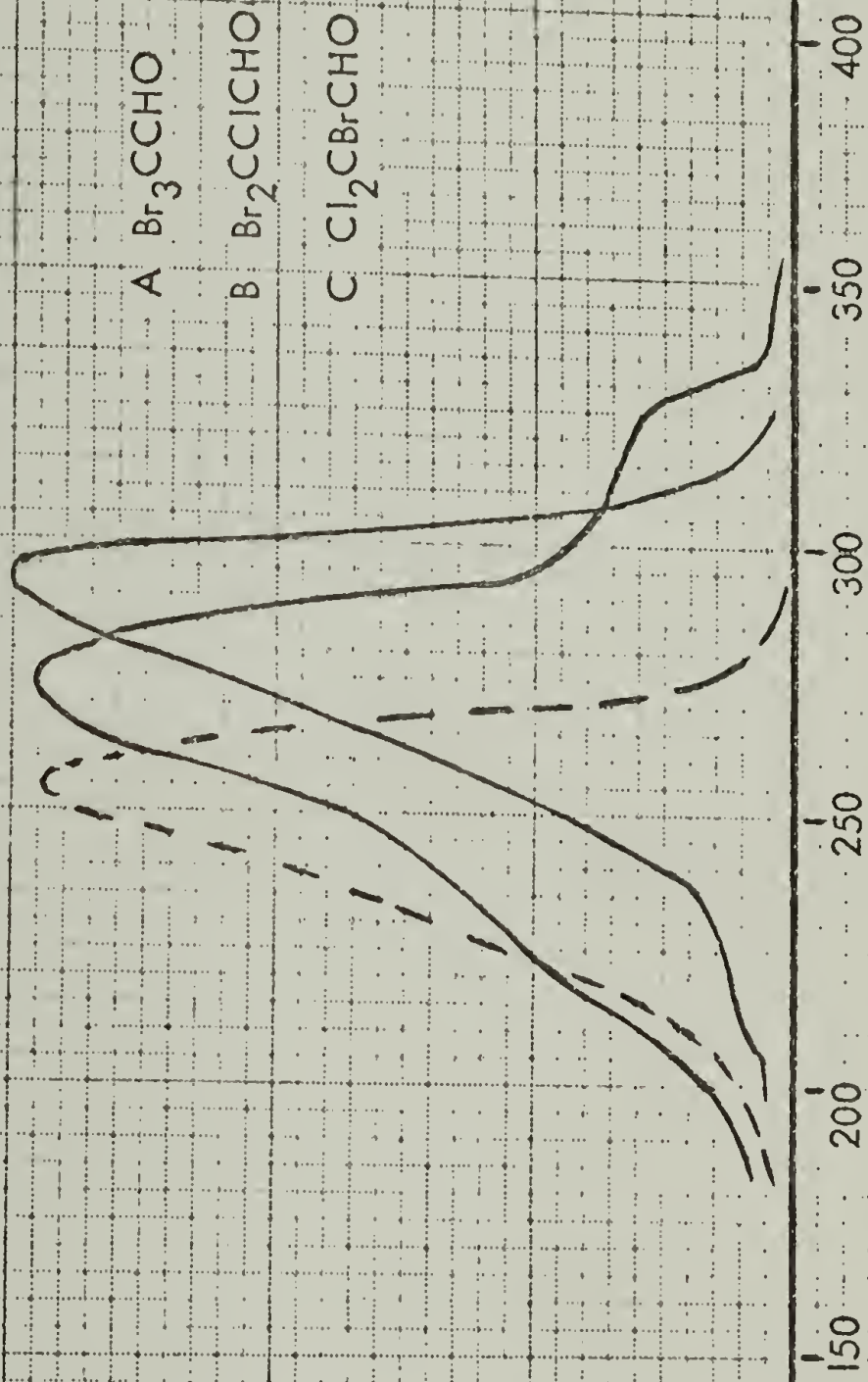


DTG CURVES OF STABILIZED  
PERHALOALDEHYDE HOMO POLYMERS

Initiator: Pyridine ( $\text{PCl}_5$  Treated)  
 $20^\circ \text{C/Min}$

A  $255^\circ$  B  $276^\circ$  C  $297^\circ$

A  $\text{Br}_3\text{CCCHO}$   
B  $\text{Br}_2\text{CCICHO}$   
C  $\text{Cl}_2\text{CBrCHO}$



RATE OF WEIGHT LOSS

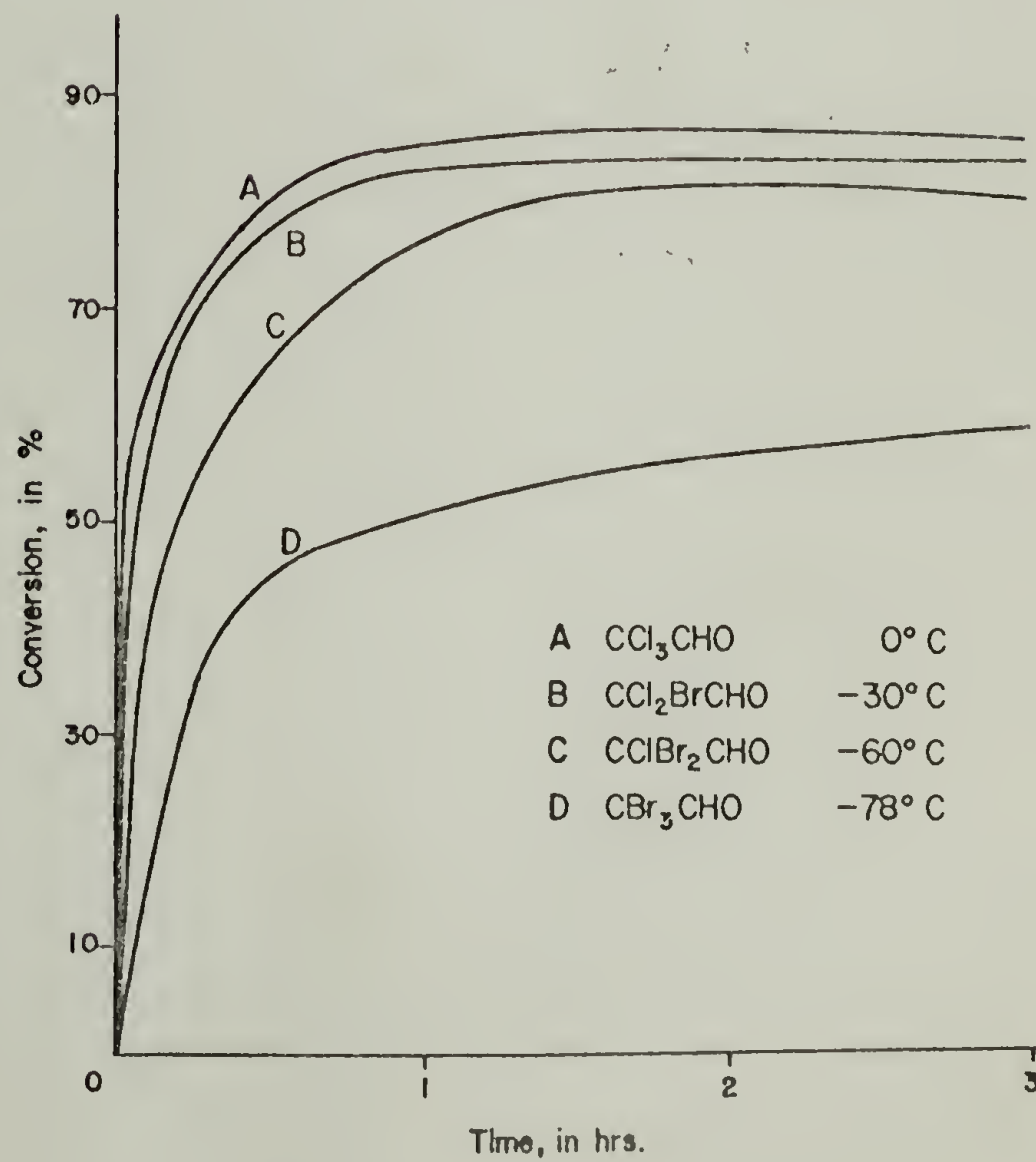
TEMPERATURE, in  $^\circ \text{C}$

# RATES OF HALOALDEHYDE POLYMERIZATION NMR STUDY

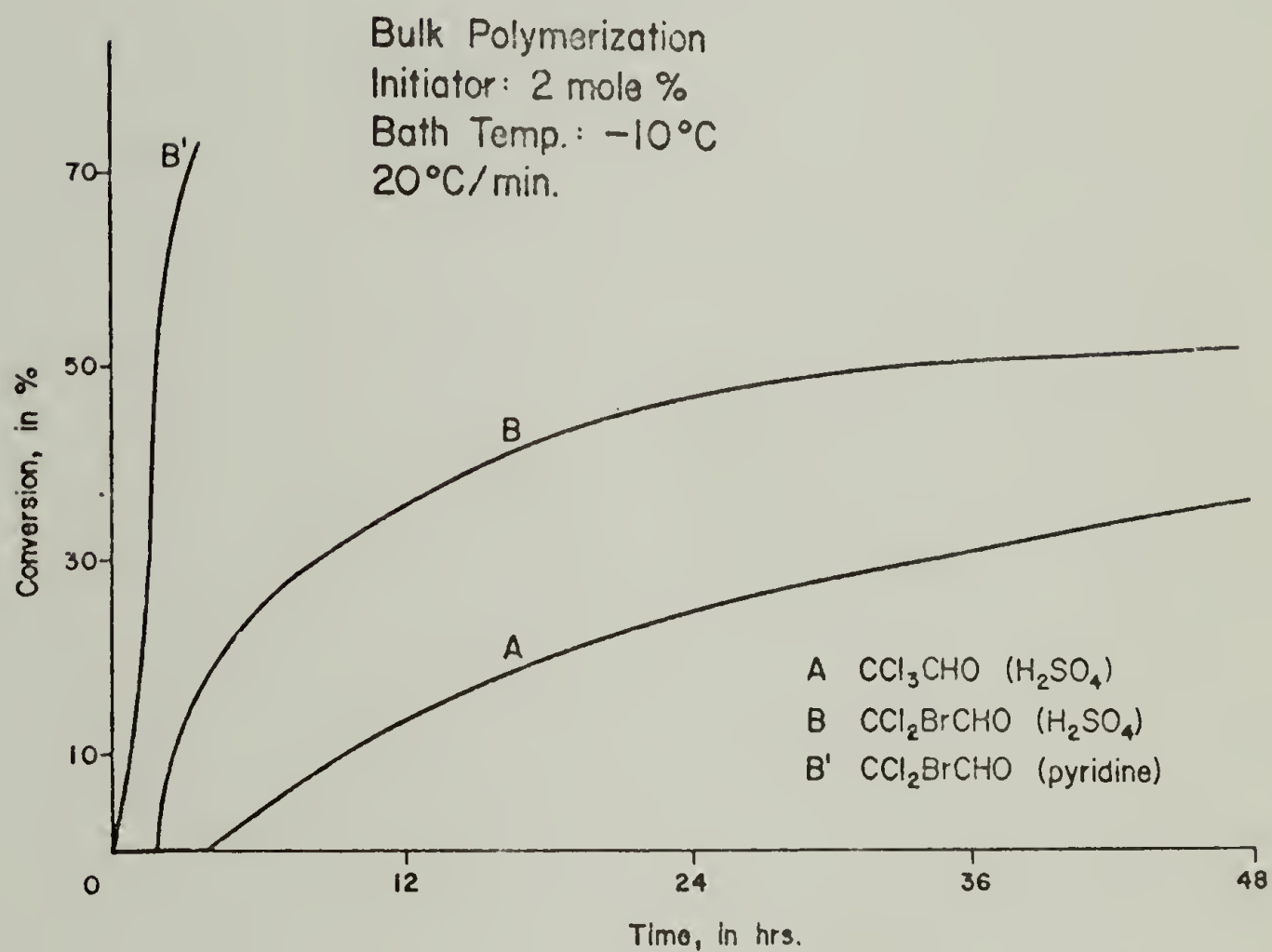
Initiator: Pyridine (2 mole%)

Monomer Conc.: 1 molar in toluene

Cooling Temp.: 10° to 20° below  $T_c$

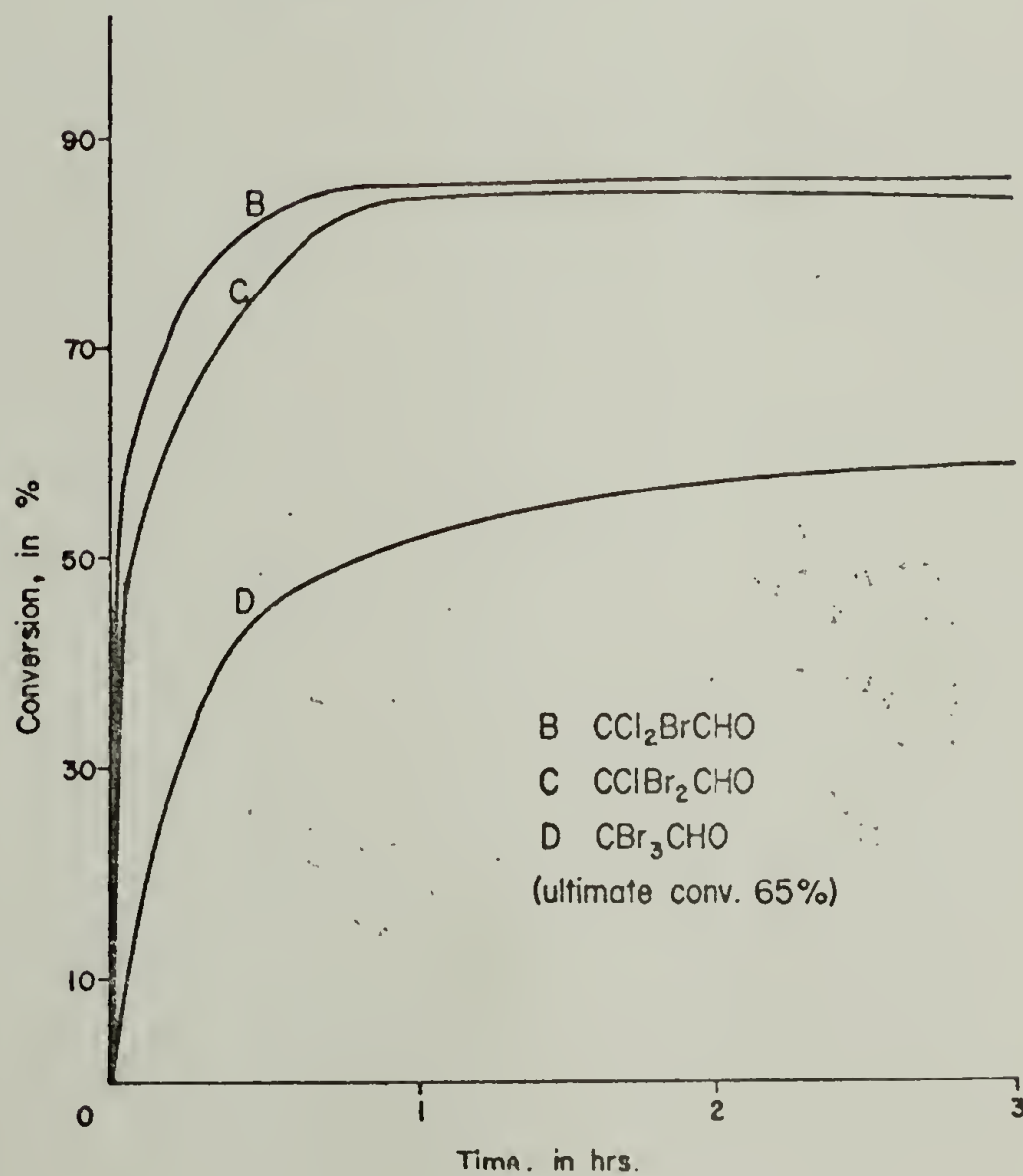


RATES OF HALOALDEHYDE POLYMERIZATION  
NMR STUDY

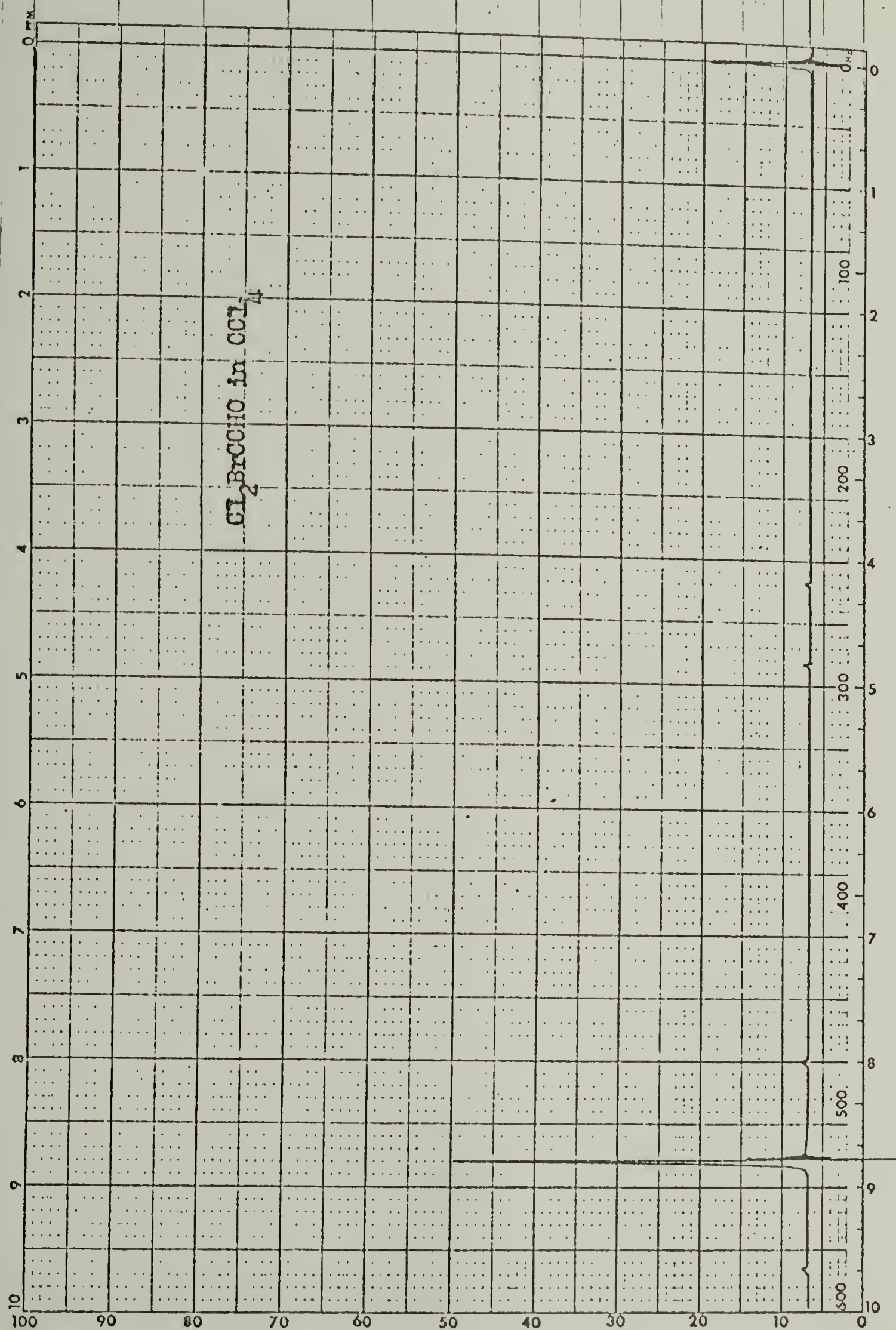


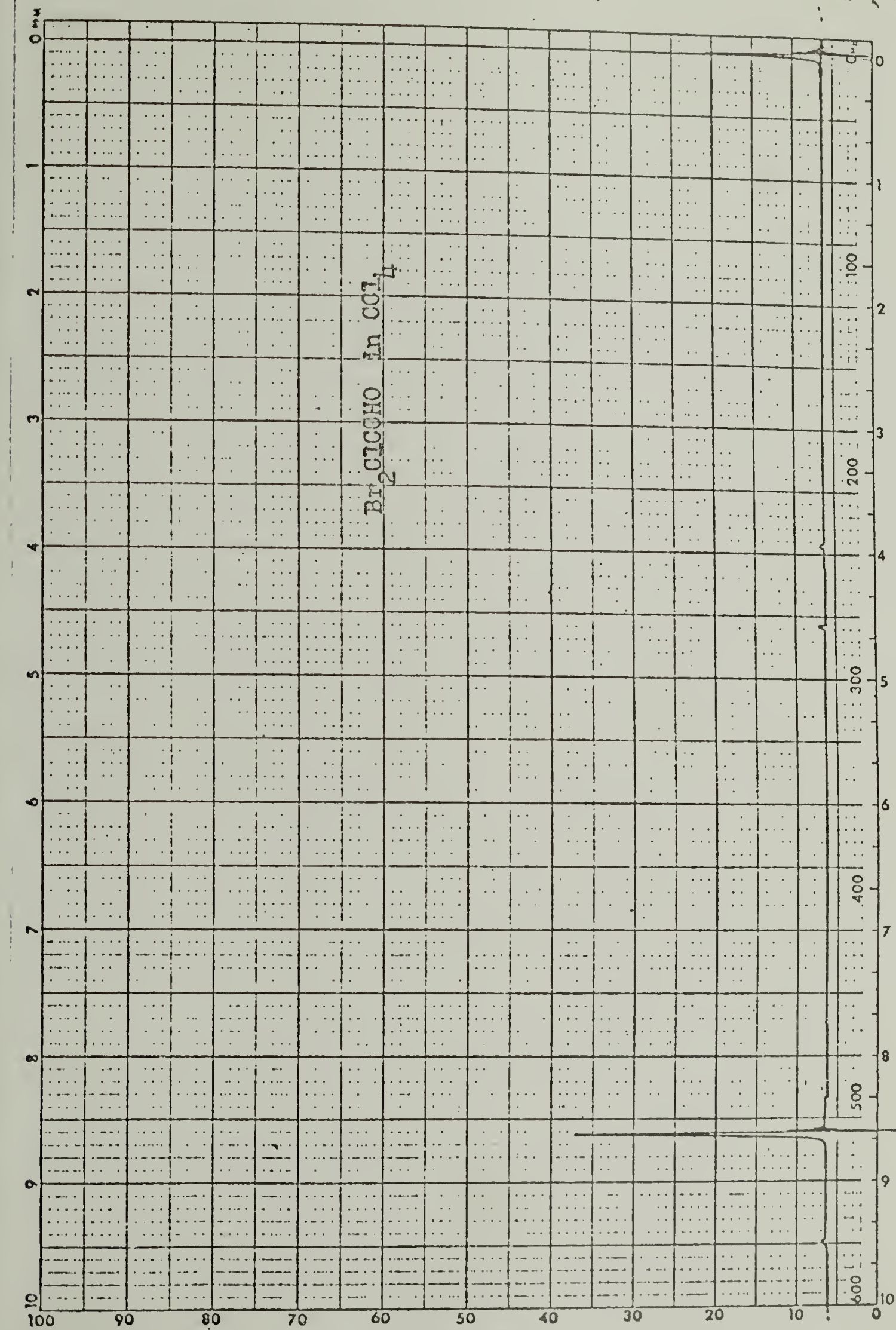
RATE OF HALOALDEHYDE POLYMERIZATION  
NMR STUDY

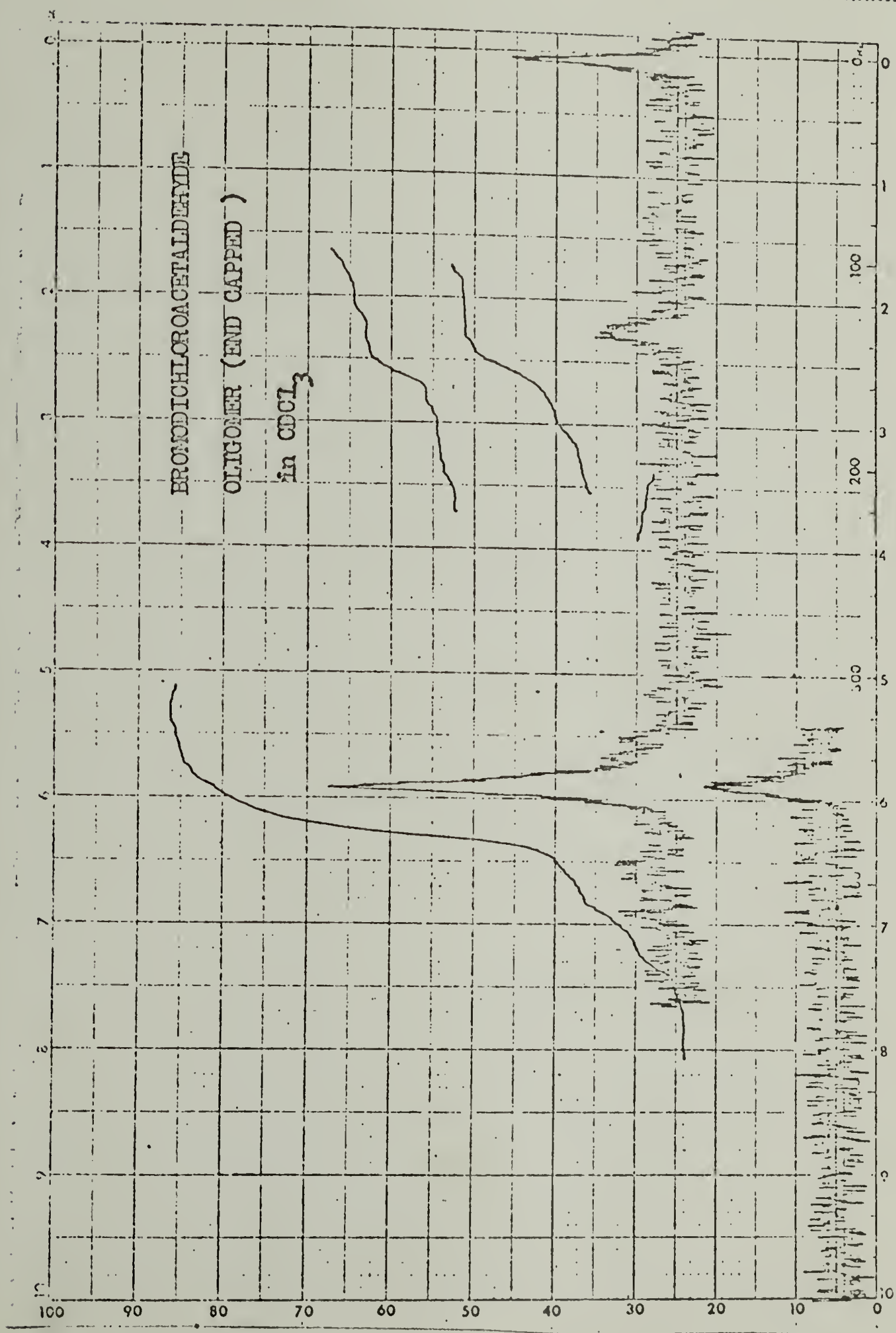
Initiator: Pyridine (2 mole %)  
Bath Temp.:  $-78^{\circ}\text{C}$   
 $20^{\circ}\text{C}/\text{min.}$





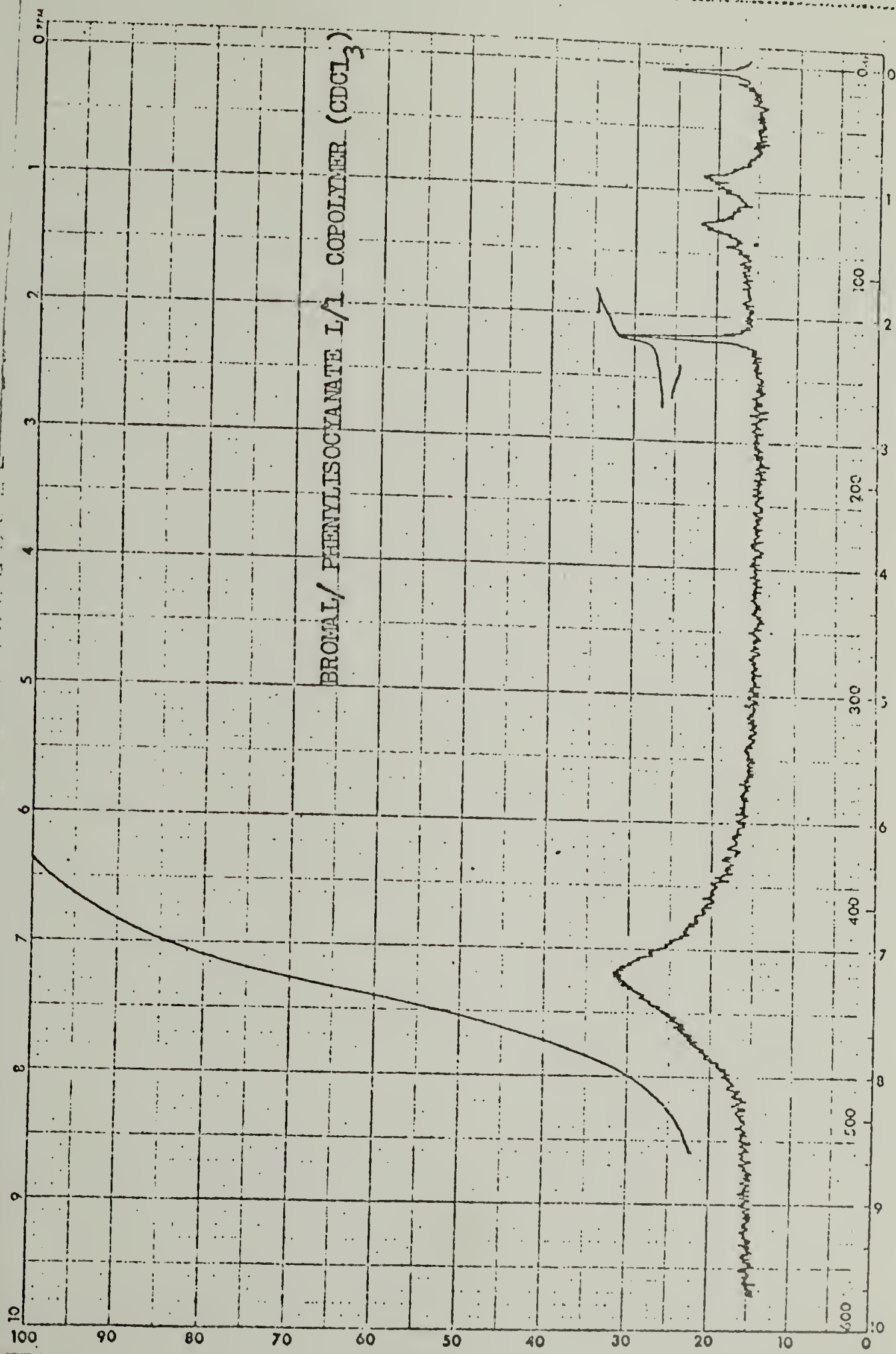




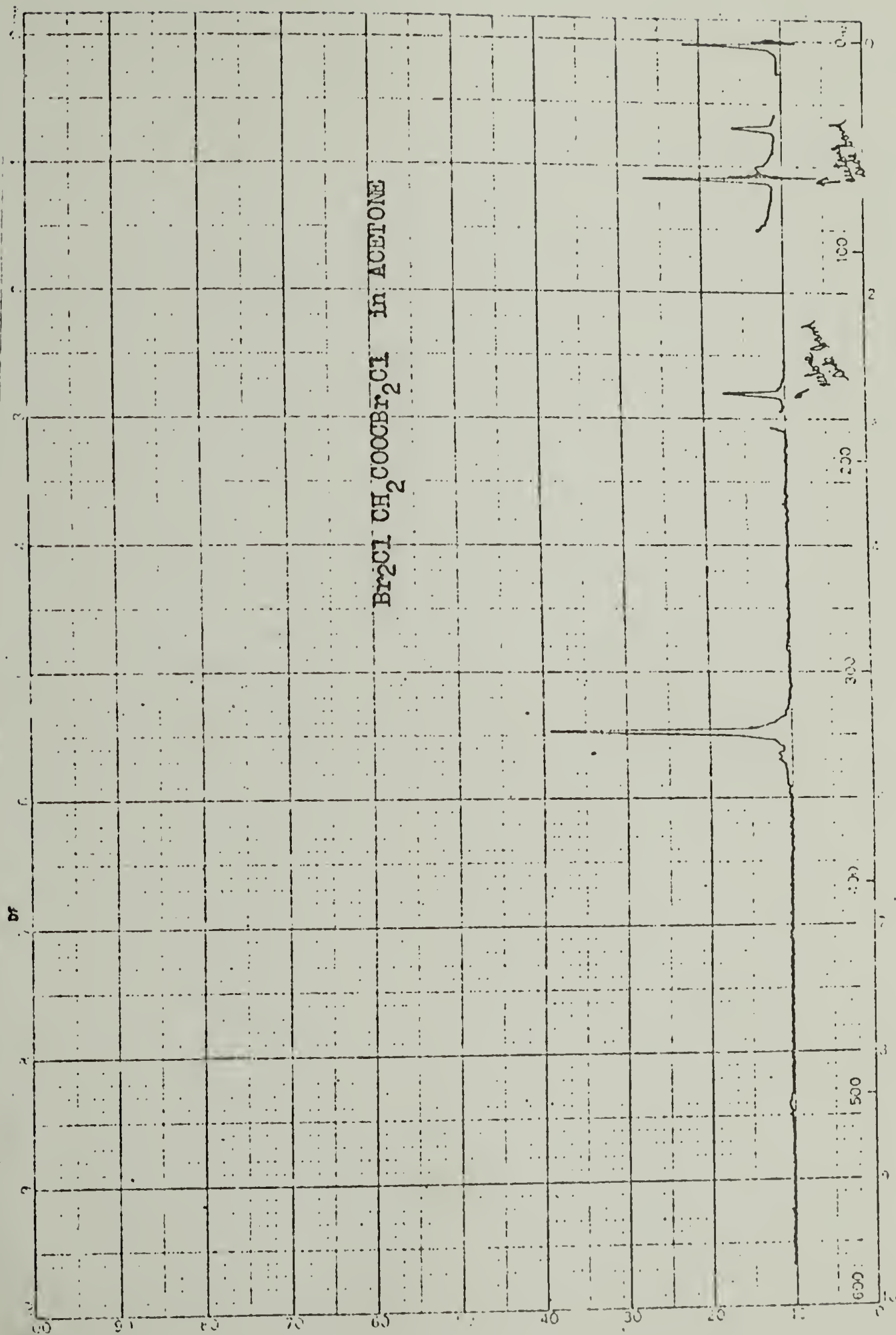




BROMAL/ PHENYLISOCYANATE 1/1 COPOLYMER (CDCl<sub>3</sub>)







APPENDIX IV - WIDE ANGLE X-RAY SCATTERING PATTERNS AND  
LOW ANGLE LIGHT SCATTERING PATTERNS

## FIGURE 3

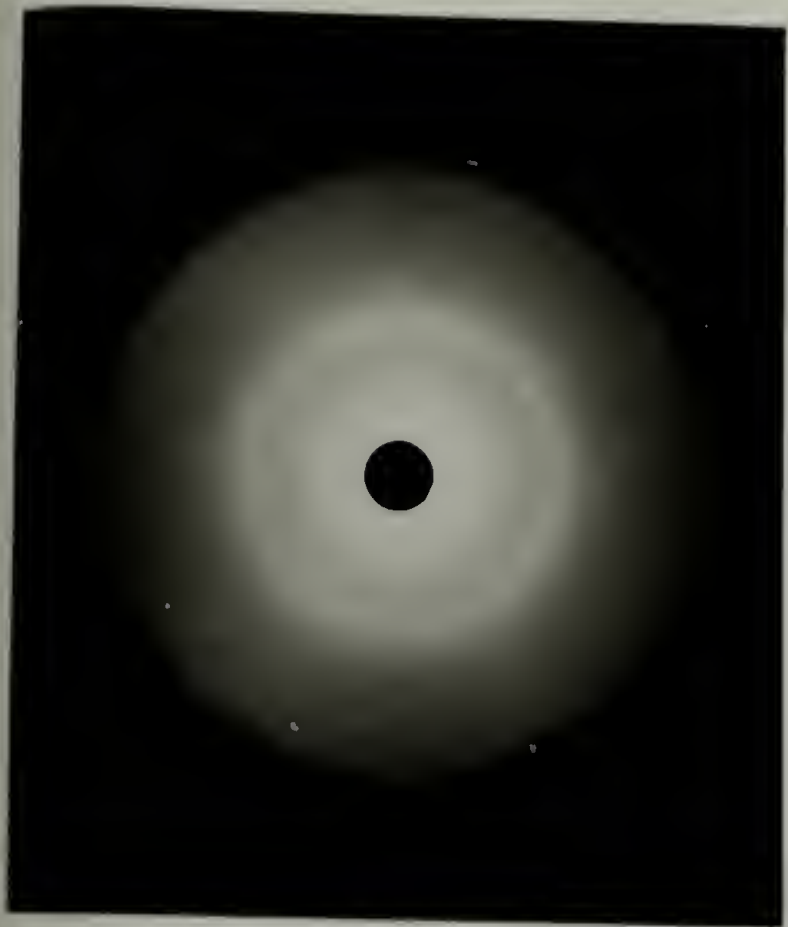
WIDE ANGLE X-RAY SCATTERING PATTERNS

A: POLYBROMAL

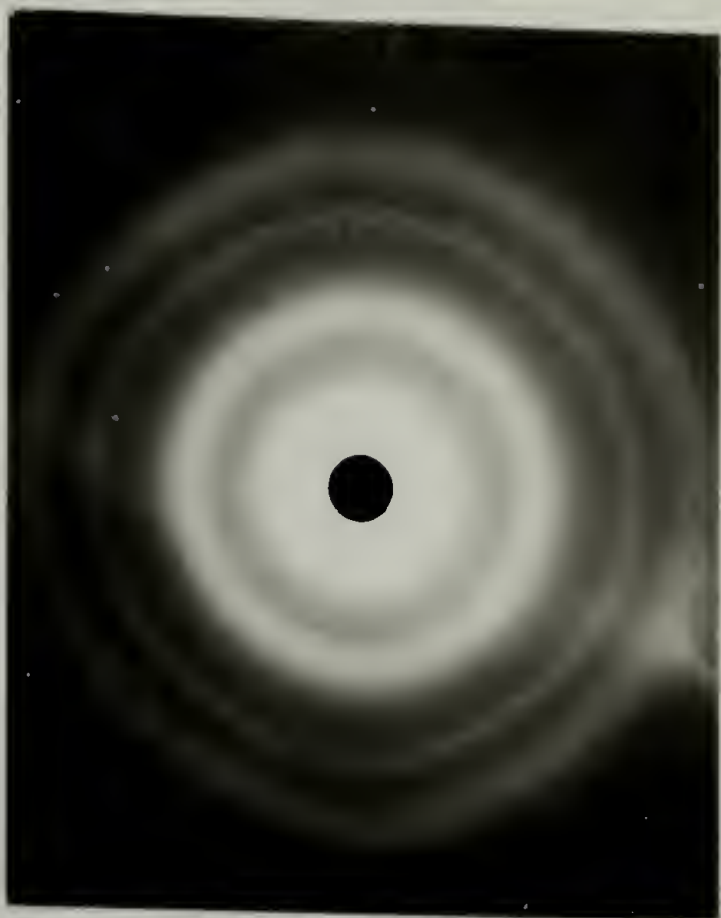
B: POLYCHLORODIBROMOACETALDEHYDE

C: POLYBROMODICHLOROACETALDEHYDE

D: BROMAL / PHENYLISOCYANATE COPOLYMER



A



B



C



D



FIGURE 1  
WIDE ANGLE X-RAY SCATTERING PATTERN OF POLYCHLORAL



FIGURE 5

LOW ANGLE POLARIZED LIGHT SCATTERING PATTERN  
FOR POLYCHLORAL A: POLARIZER VERTICAL ANALYZER  
HORIZONTAL ( $H_V$ ) B: POLARIZER VERTICAL ANALYZER  
VERTICAL ( $V_V$ )



A



B



## FIGURE 6

LOW ANGLE POLARIZED LIGHT SCATTERING PATTERN

POLARIZER VERTICAL, ANALYZER HORIZONTAL

A : POLYBROMODICHLOROACETALDEHYDE

B : CHLORAL/ BDCA COPOLYMER



A



B

## FIGURE 7

LOW ANGLE POLARIZED LIGHT SCATTERING PATTERN  
POLARIZER VERTICAL, ANALYZER HORIZONTAL  
CHLORAL/ PHENYLISOCYANATE COPOLYMER  
5% ISOCYANATE IN COPOLYMER





APPENDIX 6 PHOTOGRAPHS OF CEILING TEMPERATURE  
APPARATUS AND OF POLYCHLORAL AND POLYBROMAL  
SPACE FILLING MODELS

### Purities by Gas Chromatography

The purities of polymerization grade bromal, bromodichloroacetaldehyde and chlorodibromoacetaldehyde were determined by gas chromatography on a diisodecyl phthalate column (35% on chromosorb W) 2 meters in length.

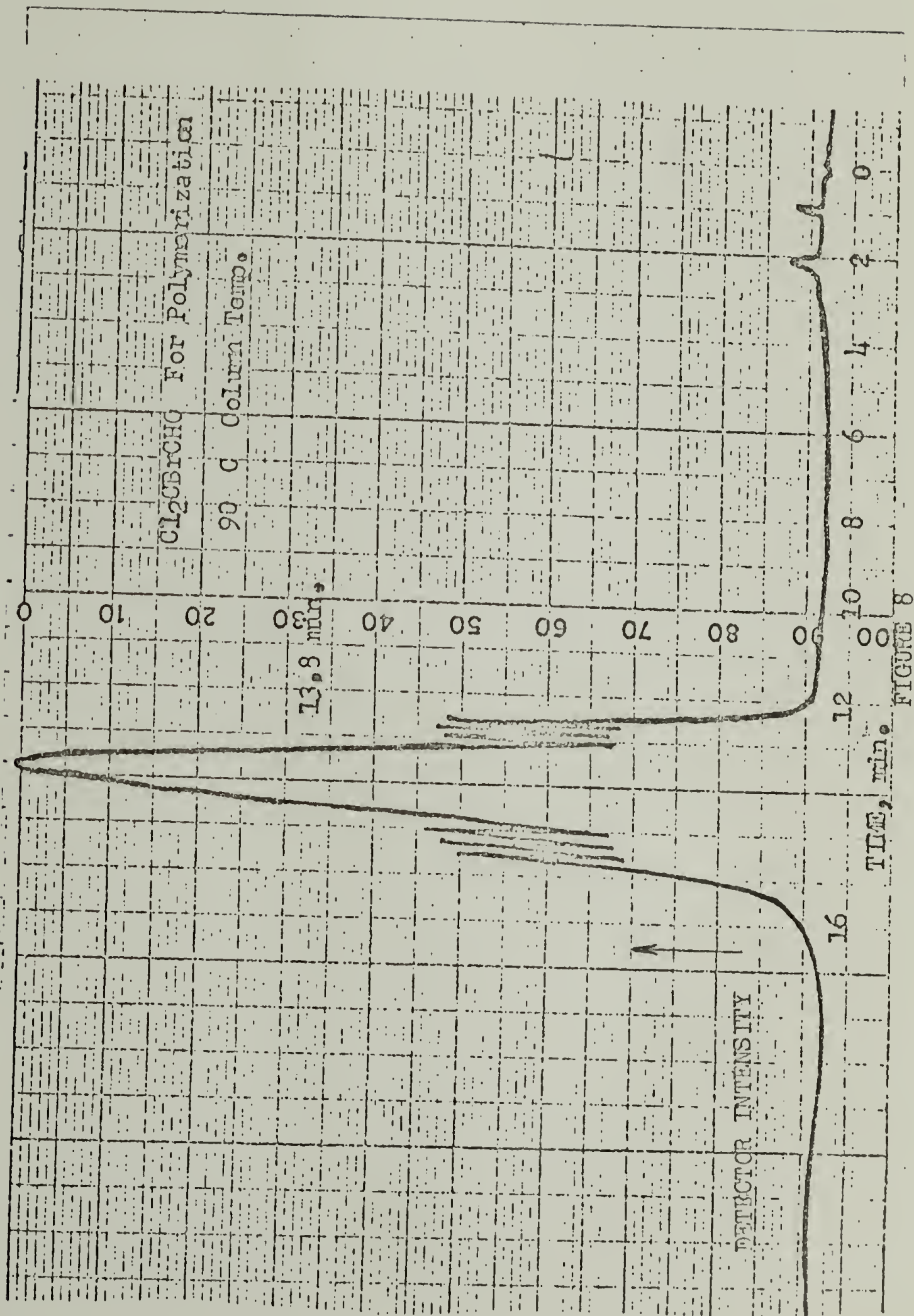
The column conditions and retention times are given in Table 6 below.

G.C. Analysis of Monomers

Monomer	Column Temperature	Retention Time	Total Impurities %
$\text{Cl}_2\text{CBrCHO}$	$90^\circ$	13 min. 48 sec.	0.2
$\text{Br}_2\text{C Cl CHO}$	$110^\circ$	15 min. 42 sec.	0.2
$\text{Br}_3\text{C CHO}$	$130^\circ$	16 min. 30 sec.	0.1

The total amount of impurities present in each monomer was determined. Purity standards were established by spiking highly purified toluene with carefully measured amounts of acetone. The sizes of the impurity peaks in the monomer chromatograms were compared with the standardized impurity peaks.

The monomer samples were submitted for gas chromatographymass spectral analysis. The GC-mass spectral analysis of the impurities was very difficult because of their low concentration. It was not possible to determine the identity of the impurities in the polymerization grade monomers.



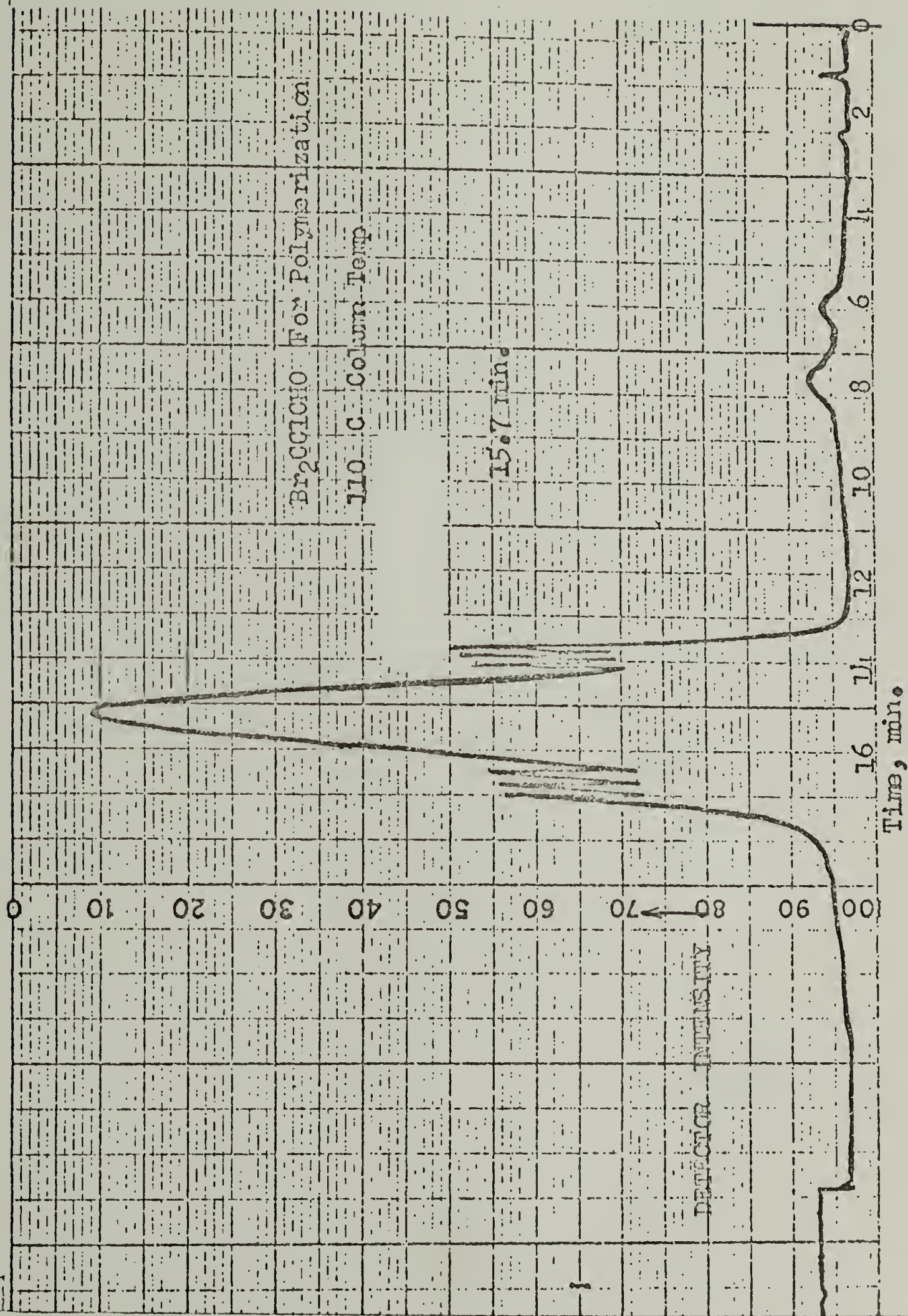


FIGURE 9



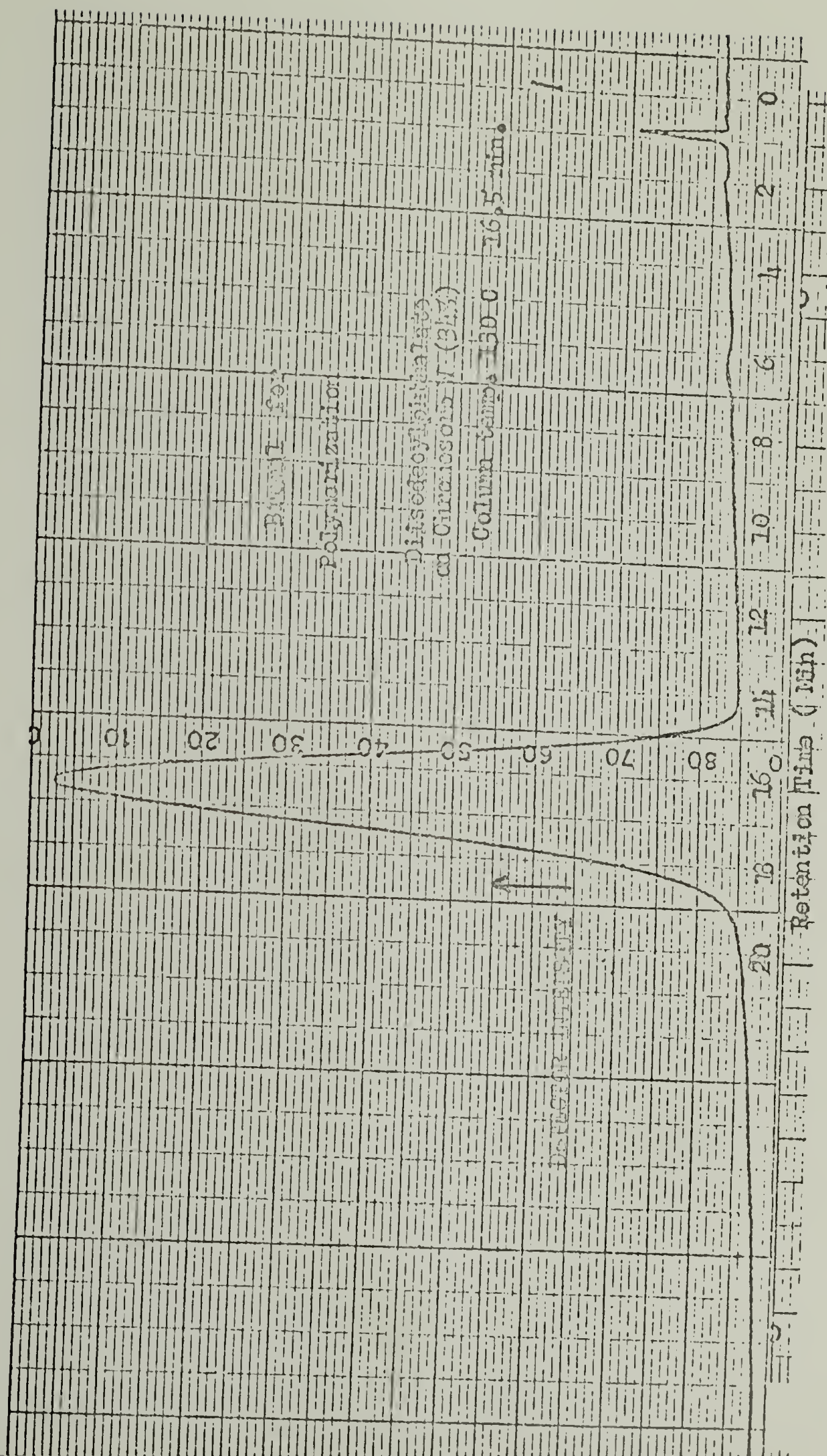
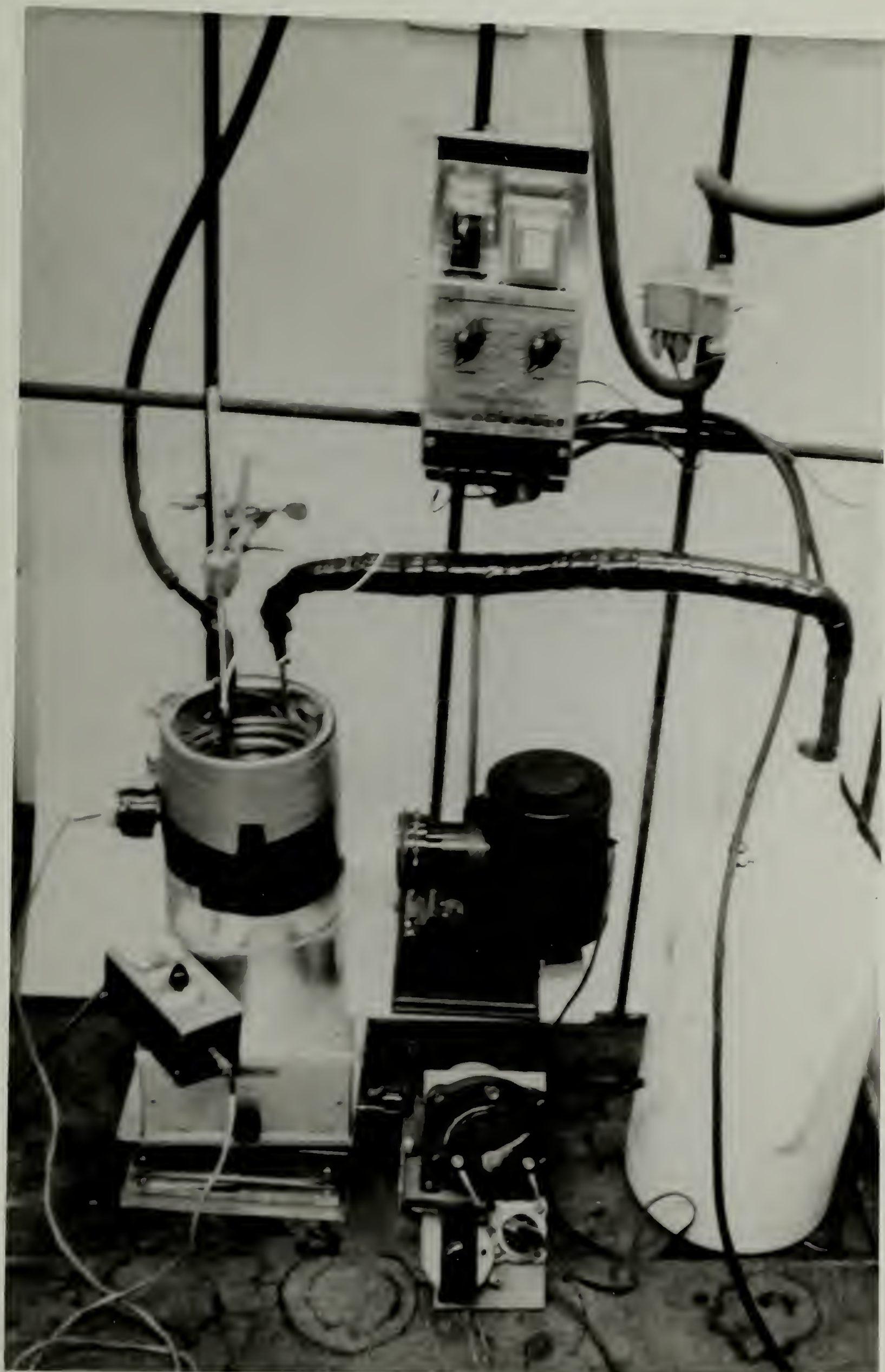


FIGURE 10

APPENDIX V .. MONOMER PURITIES BY GAS CHROMATOGRAPHY

FIGURE 11 PHOTOGRAPH OF THRESHOLD POLYMERIZATION  
TEMPERATURE APPARATUS







## FIGURE 12

PHOTOGRAPH OF A SPACE FILLING MODEL FOR POLYCHLORAL



FIGURE 13      PHOTOGRAPH OF A SPACE FILLING MODEL  
OF ISOTACTIC POLYBROMAL





